

Preliminary communication

WATER GAS SHIFT REACTION HOMOGENEOUSLY CATALYZED BY [Ir(diene)L₂]⁺ COMPLEXES

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Summary

The water gas shift reaction (WGSR) is homogeneously catalyzed by [Ir(diene)L₂]⁺ (diene = 1,5-cyclooctadiene, L and/or L₂ are mono- or bi-dentate ligands with phosphorus or nitrogen as donor atoms). The catalytic activity is compared with that of other homogeneous systems.

The water gas shift reaction (WGSR) (A) is extensively used to adjust the

$$\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad (\text{A})$$

hydrogen content of synthesis gas to be used for methanation or the Fischer—Tropsch synthesis. The equilibrium constant of reaction A increases on decreasing the temperature, and so high conversions are possible only at low temperature and very active catalysts are therefore needed.

The use as homogeneous catalysts of complexes such as [Rh(CO)₂I₂][−] in an acidic medium [1] and Ru₃(CO)₁₂ and other carbonyl clusters [2] and Fe(CO)₅ [3] in basic solution has recently been examined. We have now used [Ir(COD)L₂] complexes with mono- (L = PPh₃, PMePh₂) or bi-dentate ligands such as Ph₂P(CH₂)₂PPh₂ (DPE), phenanthroline (Phen), methyl-substituted phenanthrolines (4,7-Me₂Phen, 3,4,7,8-Me₄Phen), phenyl-substituted phenanthroline (4,7-Ph₂Phen) and the sodium salt derivative 4,7-diphenyl-phenanthroline sulfonate (PhenS). All the complexes were synthesized by slight modifications of procedures reported in the literature [4–6]. The reactions were carried out in neutral 1/1 water/dioxane solution in the case of phosphine ligands but in water in the case of other ligands. Results are reported in Table 1.

Under the reaction conditions the starting complexes react with CO with displacement of coordinated diolefin [6] to form iridium carbonyl compounds, which are the active catalytic species for the WGSR. The catalytic activity

TABLE 1

WGSR CATALYZED BY Ir^I COMPLEXES^a

Run	Complex	Concentration ($\mu \times 10^5$)	Temperature (°C)	Turnover number ^b
1	[Ir(COD)(PMePh ₂) ₂] ⁺	10	140	1.5
2	[Ir(COD)(PPh ₃) ₂] ⁺	10	140	1.5
3	[Ir(COD)DPE] ⁺	10	140	7
4	[Ir(COD)(Phen)] ⁺	7.5	140	9.5
5	[Ir(COD)(4, 7-Ph ₂ Phen)] ⁺	7.5	140	9.5
6	[Ir(COD)(4, 7-Me ₂ Phen)] ⁺	7.5	140	11
7	[Ir(COD)(3, 4, 7, 8-Me ₄ Phen)] ⁺	7.5	140	14
8	[Ir(COD)(Phen S)] ⁻	20	140	7.5
9	[Ir(COD)(Phen S)] ⁻	40	140	7
10	[Ir(COD)(Phen S)] ⁻	80	140	6.5
11	[Ir(COD)(Phen S)] ⁻	20	160	22.5
12	[Ir(COD)(Phen S)] ⁻	20	180	43.5
13	[Ir(COD)(Phen S)] ⁻	20	140	13.5 ^c

^aReaction conditions. A water-dioxane (1/1) mixture was used as solvent for runs 1–3. In the other cases water was used. The CO pressure varied over the range 6–10 atm depending on the working temperature. Both H₂ and CO₂ were determined by GLC analysis using a Porapak column and argon as carrier gas. A 190 ml autoclave was used in all the experiments. Reaction time 21 h. The complexes were used in runs 1–3 as PF₆⁻ or Cl⁻ in runs 4–7, and as sodium salts in runs 8–13.

^bTurnover number defined as mol of substrate per mol of catalyst per hour.

^cNEt₃ added, CO/NEt₃ = 1.

slightly increases when bidentate ligands are used, and appears to be rather sensitive to temperature.

Further preliminary results indicate an increase in the rate upon addition of a base (Table 1, runs 8 and 13). The complexes under investigation show, even in the absence of added acids or bases, catalytic activities comparable with those of the homogeneous catalysts previously reported for the WGSR (Table 2). Catalysis by metal carbonyls is not surprising, in the light of the well known reactivity of coordinated CO towards various nucleophiles. A possible reaction scheme is shown in Fig. 1.

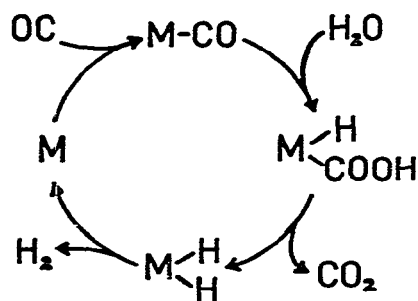


Fig. 1.

TABLE 2

WGSR CATALYZED BY VARIOUS TRANSITION METAL COMPLEXES IN SOLUTION

Complex	Temperature (°C)	p(CO) (atm)	Turnover ^a	Reference
Ru ₃ (CO) ₁₂	100	0.9	2.7	2
Ru ₃ (CO) ₁₂	150	23.8	8000	7
Rh ₆ (CO) ₁₆	100	0.9	1.3	2
[Rh(CO) ₂ I ₂] ⁻	100	0.5	36	1
Fe(CO) ₅	180	40	2000	3
[Ir(COD)(PhenS)] ⁻	180	10	1000	this work

^aTurnover number expressed in mol of substrate per mol of catalyst per day.

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