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HYDROGEN TRANSFER REACTIONS CATALYZED BY RHODIUM(III)- AND IRIDIUM(III)-TIN(II) SYSTEMS

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Summary

The hydrogen transfer reaction from isopropanol to cyclohexanones is catalyzed by rhodium(III)- and iridium(III)-tin(II) systems. The influence of various parameters such as Sn^{II}/M^{III} ratio, $[H^+]$ and $[Cl^-]$ on the reaction rate and on the stereoselectivity has been examined.

Introduction

The catalytic activity of transition metal compounds-tin chloride systems for hydrogenation of organic substrates is well known, and the subject has been recently reviewed [1]. Among several other systems, platinum group metals have been studied following the discovery of the effectiveness of stannous chloride in promoting the catalytic activity of platinum chloride for olefin hydrogenation [2]. Kinetic studies on olefin hydrogenation catalyzed by platinum-tin complexes showed that catalytic activity in these reactions depends on the tin/platinum ratio, reaching a maximum for values higher than five [3]. Moreover, coordination of ethylene to platinum is catalyzed by the presence of tin chloride. In fact, while formation of Zeise's salt from $PtCl_4^{2-}$ and ethylene is rather slow, it is markedly accelerated by the presence of $SnCl_2 \cdot 2\,H_2O$ [4,5]. A kinetic study of this reaction showed [6] that this effect is probably related to the high *trans* effect and to the pronounced π-acceptor character of $SnCl_3^-$ bonded to platinum(II). Chloro complexes of rhodium(III) catalyze the dehydrogenation of isopropanol to acetone with hydrogen evolution [7]. The reaction probably proceeds via transfer of a hydride group from the α-carbon atom of the alcohol to the rhodium complex. The rhodium hydride intermediate formed reacts with a proton present in the solution to form hydrogen, or decomposes to give rhodium metal, according to the following equations:

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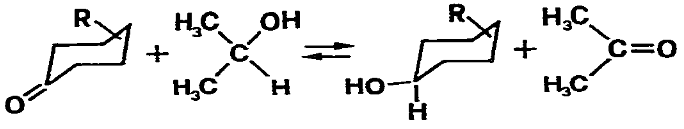
$Me_2CHOH + [RhCl_6]^{3-} \rightleftharpoons Me_2CO + [HRhCl_5]^{3-} + HCl$

$HCl + [HRhCl_5]^{3-} \rightleftharpoons H_2 + [RhCl_6]^{3-}$

$[HRhCl_5]^{3-} \rightarrow$ Rh metal

Addition of tin chloride stabilizes the rhodium intermediate and no precipitation of metal occurs under these conditions [8]. The complex formed from rhodium(III) chloride and tin(II) chloride was isolated and formulated as $[Rh_2(SnCl_3)_4Cl_2]^{4-}$ [9]. We suspect, however, that more than one species may be present in the catalytic solution, and indeed, the isolated rhodium dimer does not appear to be a good catalyst for the hydrogen transfer reaction. Higher yields of hydrogen obtained by alcohol dehydrogenation can be reached using the same rhodium-tin system under irradiation from a low pressure lamp [10] or using ruthenium or osmium complexes of the type $M(OCOR_F)_2(CO)(PPh_3)_2$ [11]. We have used rhodium and iridium-tin systems to catalyze hydrogen transfer reaction from isopropanol to cyclic ketones such as cyclohexanone or substituted cyclohexanones:



(1)

R = H, 4-tert-butyl, 2-, 3-, 4-methyl

We have investigated the effect on the reaction of several parameters such as concentration of added acid or chloride and the ratio rhodium or iridium/tin. The effect of the substituent R has also been examined.

Results and discussion

We used as catalysts for reaction 1 the $MCl_3 \cdot 3\ H_2O$ (M = Rh and Ir) or H_3IrCl_6 and $SnCl_2 \cdot 2\ H_2O$ systems in the presence of added HCl and/or LiCl as source of chloride. Under these conditions several species are formed in solution from $SnCl_2$ and Cl^- according to the following equilibria:

$$Sn^{2+} + Cl^- \rightleftharpoons SnCl^+$$

$$SnCl^+ + Cl^- \rightleftharpoons SnCl_2 \qquad (2)$$

$$SnCl_2 + Cl^- \rightleftharpoons SnCl_3^-$$

$$SnCl_3^- + Cl^- \rightleftharpoons SnCl_4^{2-}$$

$SnCl_3^-$ readily coordinates to transition metals to form complexes in which it acts as a good π-acceptor ligand [12], and moreover it stabilizes complexes towards reduction to metal [8]. We have studied the influence of adding different amounts of $SnCl_2 \cdot 2\ H_2O$, HCl and LiCl to $MCl_3 \cdot 3\ H_2O$ (M = Rh, Ir) or H_3IrCl_6 solutions in isopropanol on the catalytic hydrogen transfer from

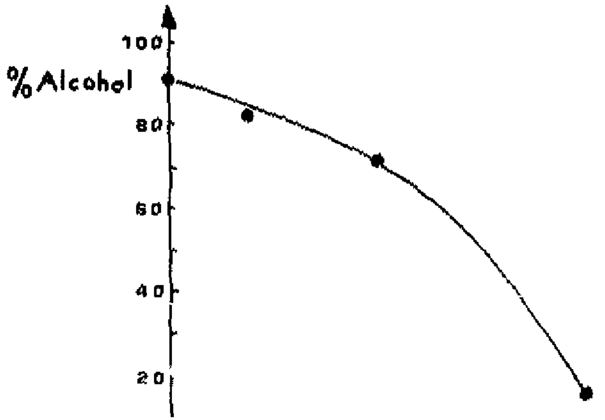
TABLE 1

EFFECT OF THE ACID AND OF THE CHLORIDE CONCENTRATION ON THE REDUCTION OF 4-tert-BUTYLCYCLOHEXANONE [a]

	Run	[HCl] (*M*)	HCl/ $MCl_3 \cdot 3\,H_2O$	[LiCl] (*M*)	LiCl/ $MCl_3 \cdot 3\,H_2O$	% alcohol	% *cis* isomer	*r* [b]
M = Ir	1 [c]	0.52	68.4	0	0	93.5	91	28
	2	0.26	34.2	0	0	90	90	27
	3	0.26	34.2	0.104	13.7	81	89	24
	4 [c]	0.26	34.2	0.26	34.2	71	81	21
	5	0.26	34.2	0.52	68.4	16	58	5
	6	0.104	13.7	0	0	65	93	19
	7 [c]	0.104	13.7	0.416	54.7	33.5	89	10
	8	0.052	6.8	0	0	34	90	10
	9 [c]	0.052	6.8	0.468	61.6	24	92	7
	10	0	0	0	0	17	74	5
	11 [c]	0	0	0.52	68.4	7	~90	2
M = Rh	12	0.52	68.4	0	0	31	55	9
	13	0.26	34.2	0	0	23	55	7
	14 [c]	0.26	34.2	0.26	34.2	23	63	7
	15	0.104	13.7	0	0	1	69	5
	16 [c]	0.104	13.7	0.416	54.7	15	74	4
	17	0.052	6.8	0	0	10	80	3
	18	0	0	0	0	3	~90	1.5
	19 [c]	0	0	0.52	68.4	5	~90	1.5

[a] Reaction conditions 4-tert-butylcyclohexanone in refluxing isopropanol (83°C) Substrate/catalyst ratio = 150. Reaction time 5 hours. $[MCl_3 \cdot 3\,H_2O]$ (M = Ir, Rh) = 7.6×10^{-3} *M*, $[SnCl_2 \cdot 2\,H_2O]$ = 22.8×10^{-3} *M* [b] r = (moles of product) × (moles of $MCl_3 \cdot 3\,H_2O)^{-1}$ × (hours)$^{-1}$ [c] [HCl] + [LiCl] is kept constant at 0.52 *M*

the solvent to cyclic ketones (see eq. 1) to give the corresponding alcohols. The results for reduction of 4-tert-butylcyclohexanone are reported in Table 1. Iridium-based catalysts are more active than rhodium species, and the selectively is much higher. The substrate/catalyst ratio is not very high (see Table 5),



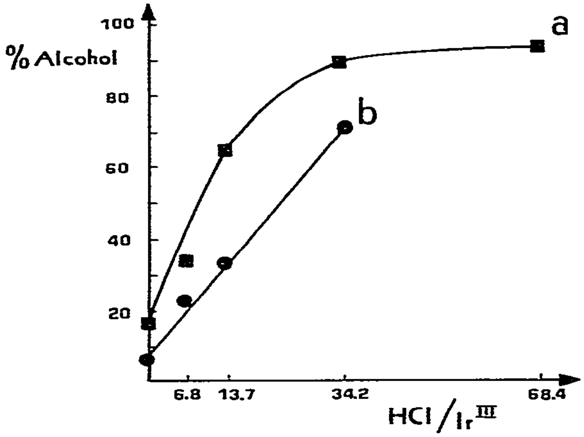


Fig. 2. Effect of the acid and the chloride concentration on the reduction of 4-tert-butylcyclohexanone (a: no LiCl added, b: [HCl] + [LiCl] was kept constant at 0.52 *M*). Reaction conditions as shown in Table 1 for the iridium(III) system.

especially when compared to values of 10^5 we used with iridium-phosphine catalysts to reduce the same substrates [14]. The rate of reduction is very dependent on the chloride ion concentration. Addition of LiCl at constant HCl concentration decreases the yield in alcohol, which drops from a value of 90% (run 2, Table 1, no LiCl added) to a value of 16 (run 5 and Fig. 1). At the same time also the selectivity appears to be dependent on the concentration of chloride. The percentage of *cis* isomer, which reaches the value of 91% (run 1), decreases to the value of 58% (run 5), increasing [Cl^-]. In runs 1, 4, 7, 9 and 11, [HCl] + [LiCl] is kept at the constant value of 0.52 *M* but [HCl] is decreased at the same time; under these conditions the extent of conversion after 5 hours of reaction drops from 93.5% to 7% (Fig. 2, curve b). The selectivity towards the *cis* isomer, however, remains practically the same, showing that while chloride concentration plays an important role both on rate and on selectivity,

TABLE 2

EFFECT OF $SnCl_2 \cdot 2\ H_2O/MCl_3 \cdot 3\ H_2O$ RATIO (M = Ir, Rh) ON THE REDUCTION OF 4-tert-BUTYLCYCLOHEXANONE AT CONSTANT HCl CONCENTRATION [a]

	Run	$SnCl_2 \cdot 2\ H_2O/$ $MCl_3 \cdot 3\ H_2O$	% alcohol	% *cis* isomer	r [b]
M = Ir	1	3	93.5	91	28
	2	4	82	93	24.5
	3	5	81	92.5	24
	4	6	60	94	18
	5	10	7	~90	2
M = Rh	6	3	31	55	9
	7	6	19	83	6
	8	10	13	87	4

[a] Reaction conditions: 4-tert-butylcyclohexanone in refluxing isopropanol (83°C). Substrate/catalyst ratio = 150. Reaction time: 5 hours. [$MCl_3 \cdot 3\ H_2O$] (M = Rh, Ir) = 7.6×10^{-3} *M*. [HCl] 0.52 *M*. [b] r = (moles of product) × (moles $MCl_3 \cdot 3\ H_2O)^{-1}$ × (hours)$^{-1}$.

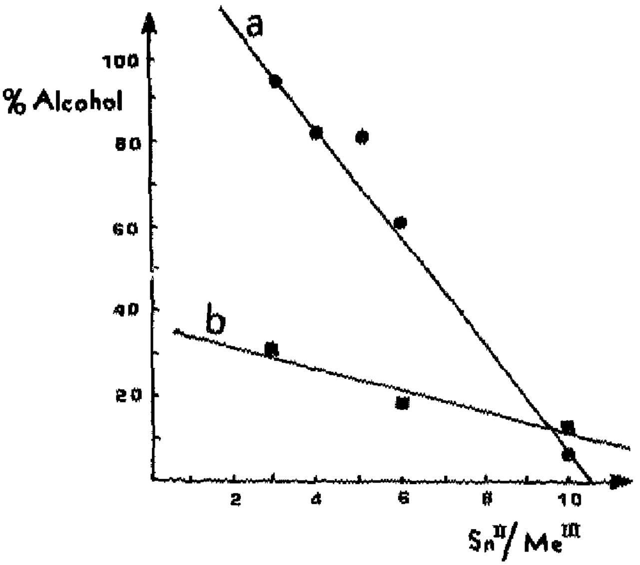


Fig. 3. Effect of the $SnCl_2 \cdot 2H_2O/MCl_3 \cdot 3H_2O$ (M = Ir curve a and Rh curve b) ratio on the reduction of 4-tert-butylcyclohexanone. Reaction conditions as shown in Table 2.

acid concentration has no influence on the selectivity.

The rhodium system appears to be more complex. Upon decreasing the acid concentration, the rate decreases as expected, but at the same time the selectivity increases (runs 12, 13, 15 and 17). Upon keeping chloride concentration constant, but varying the [HCl] (runs 14, 16 and 19), the selectivity in rhodium system increases from 63% to 74% to 90%. This behaviour is the opposite of that expected from that for the iridium system. Changing the tin(II)/metal(III) ratio also affects the two systems differently (Table 2). In both cases the reaction is slower with increasing the Sn^{II}/Me^{III} ratio (Fig. 3), but the effect is much greater in the iridium than in the rhodium system. The selectivity is also affected, and it increases with the increasing ratio; the effect on the rhodium system is very large, whereas with iridium system, since the selectivity is already high, the effect appears to be rather small when expressed in terms of increased percentage of *cis* alcohol. Interpretations of all these results must probably be based on the equilibria present in the solution and

TABLE 3

REDUCTION OF METHYLCYCLOHEXANONES [a]

	Substrate	% alcohol	% OH axial isomer	*r* [b]
M = Ir	2-Methylcyclohexanone	27	90	8
	3-Methylcyclohexanone	93	80	28
	4-Methylcyclohexanone	94	79	29
M = Rh	2-Methylcyclohexanone	9.5	~90	3

TABLE 4

REDUCTION OF CYCLOHEXANONE WITH H_3IrCl_6 AS CATALYST PRECURSOR [a]

Run	[HCl] (*M*)	Sn^{II}/Ir^{III}	% alcohol	r [b]
1	0.104	3	94	117
2	0.104	4	78	97
3	0.104	6	40	50
4	0.104	10	3.5	4
5	0.052	3	85	106
6	0.0208	3	66	82
7	0	3	9	11

[a] Reaction conditions: cyclohexanone in refluxing isopropanol (83°C). Substrate/catalyst ratio: 500. Reaction time: 4 hours. $[H_3IrCl_6] = 1.52 \times 10^{-3}$ *M*. [b] r = (moles of product) × (moles of $H_3IrCl_6)^{-1}$ × $(\text{hours})^{-1}$.

the several species which could possibly be formed. For example, the $SnCl_3^-$ concentration will be different if the Cl^- concentration is changed (see equilibria 2) and this might affect both the reaction rate and the selectivity of the catalyst. Moreover, chloride ion can compete for the same metal center with the substrate and/or hydrogen donor, reducing the actual concentration of active species. Steric hindrance plays an important role in these reactions as shown in Table 3, where the reduction of differently substituted cyclohexanones is reported. As expected, the iridium-based system is more active than the rhodium one, and the rate of reduction in both cases follows the sequence 2-methylcyclohexanone < 3-methylcyclohexanone ⩽ 4-methylcyclohexanone. It appears that the most sterically demanding substrate coordinates in such a way that a higher amount of the OH axial isomer is obtained.

Cyclohexanone was also reduced and the influence of the reaction conditions and of the nature of the procatalyst were studied. The results are reported in Table 4. As always in our work, the iridium system was found to be the more

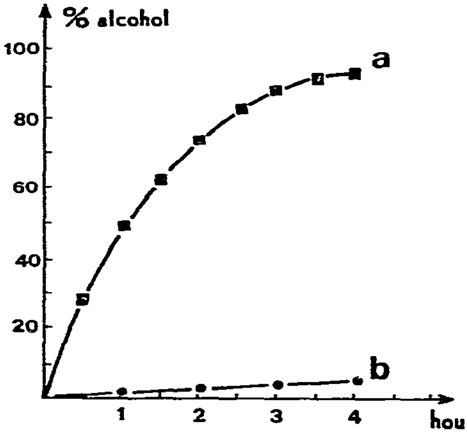
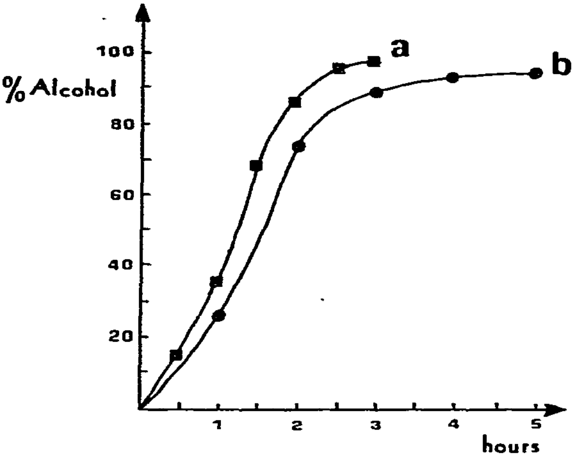


Fig. 4. Reduction of cyclohexanone using $H_3IrCl_6 \cdot nH_2O$ (curve a) and $RhCl_3 \cdot 3\ H_2O$ (curve b) as catalyst precursors. Reaction conditions as shown in Table 4, run 1.



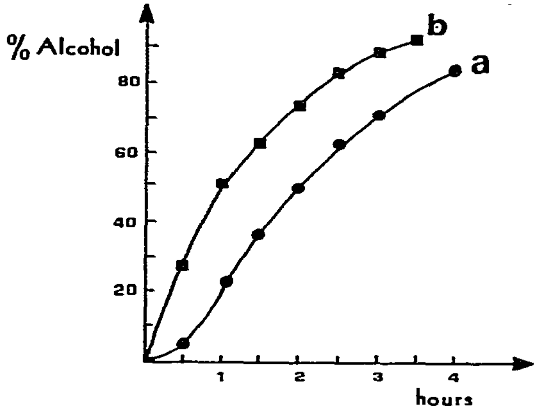


Fig. 5. Reduction of 4-tert-butylcyclohexanone using $H_3IrCl_6 \cdot nH_2O$ (curve a) and $IrCl_3 \cdot 3\ H_2O$ (curve b) as catalyst precursors. Reaction conditions as shown in Table 1, run 1.

Fig. 6. Effect of the induction time on the reduction of cyclohexanone. a) induction period 0 minutes; b) induction period 60 minutes. Reaction conditions as shown in Table 4, run 1.

active, and its activity with respect to the rhodium system is much higher than usual (Fig. 4).

Upon using $H_3IrCl_6 \cdot nH_2O$ as procatalyst to reduce cyclohexanone and 4-tert-butylcyclohexanone, we observed that the general behaviour appears to be rather similar to that found for $IrCl_3 \cdot 3\ H_2O$ (Fig. 5), suggesting that the catalytic species involved in the two cases are (or is) essentially the same. The higher reaction rate for the $H_3IrCl_6 \cdot nH_2O$ system could be due to different induction periods and/or to different concentration of active species in the two systems. An induction period is normally present (Fig. 6), but is disappears when the system is refluxed for an hour before addition of the substrate, and we think that this time is necessary for complete formation of the active species. For sake of comparison, Table 5 gives some of the results available in the literature for the hydrogen transfer reduction of cyclohexanone. This system

TABLE 5

REDUCTION OF CYCLOHEXANONE BY HYDROGEN TRANSFER REACTION CATALYZED BY SOME TRANSITION METAL COMPLEXES

Catalyst [a]	Substrate/catalyst	% Conversion (time, h)	r [b]	Ref.
$IrCl_3(DMSO)_3$	300	97 (72)	4	15
$RhCl(PPh_3)_3$	1900	59 (0.25)	4500	17
$[Rh(COD)(DPE)]^+$	1900	90 (0.25)	6800	17
$[Ir(COD)(3,4,7,8\text{-}Me_4Phen)]^+$	39700	95 (3)	12570	16
$[Ir(COD)(PPh_3)_2]^+$	30000	52 (0.07)	243000	14
$H_3IrCl_6\text{-}SnCl_2 \cdot 2\ H_2O$	500	94 (4)	117	this work

[a] DMSO = dimethylsulfoxide; COD = 1,5-cyclooctadiene; DPE = 1,2-diphenylphosphinoethane; Phen = phenanthroline. [b] r = (moles of product) X (moles of complex)$^{-1}$ X (hours)$^{-1}$.

does not seem to be competitive in terms of rate with iridium and rhodium cationic systems (see Table 5), but the reaction conditions are very different, with respect to the nature of cocatalysts, the "activation" of procatalysts, etc.

Experimental section

Catalyst precursors ($H_3IrCl_6 \cdot nH_2O$, $IrCl_3 \cdot 3\ H_2O$, and $RhCl_3 \cdot 3\ H_2O$) and reagents ($SnCl_2 \cdot 2\ H_2O$, HCl and LiCl) were used without further purification. Isopropanol was distilled and stored under nitrogen before use. 4-tert-Butylcyclohexanone was crystallized from MeOH, cyclohexanone and substituted cyclohexanones were purified by low pressure distillation.

The reaction products were analyzed by GLC using a DANI 3400 apparatus. Reactions were carried out by two different methods (a) and (b), but both gave similar results.

a) To a 10 ml HCl solution in isopropanol, the catalyst precursors ($MCl_3 \cdot 3H_2O$ or $H_3IrCl_6 \cdot nH_2O$, $SnCl_2 \cdot 2H_2O$), LiCl and the substrate were added in the appropriate ratios. The solution was refluxed with stirring for 5 hours, and then analyzed by GLC.

b) The reaction was carried out under nitrogen. A solution of HCl in isopropanol (50 ml) containing the catalyst precursors and LiCl was refluxed, with stirring, for 60 minutes, and the substrate was then added. The reaction was carried on for a period of 4 hours, samples being taken periodically for analysis by GLC.

Acknowledgments

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