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Catalysis Today 100 (2005) 467–471

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Cis–trans isomerization of olefinic alcohols promoted by Rh(I) complexes

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Abstract

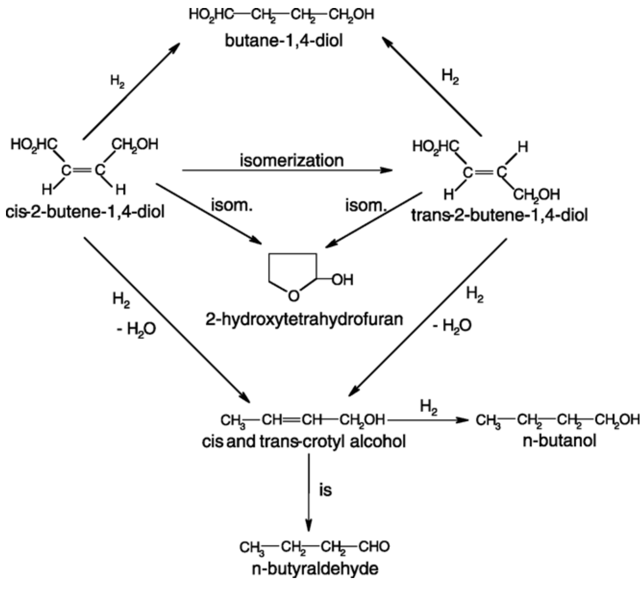
Homogeneous hydrogenation and isomerization reaction of *cis*-2-butene-1,4-diol has been investigated in ethanol by using tris(triphenylphosphine)chlororhodium(I), $RhCl(PPh_3)_3$, and triethylamine at 303 K and 0.01–0.1 MPa partial hydrogen pressure. Under reduced H_2 pressure, the geometric isomerization reaction occurs, to a high extent, leading to *trans*-2-butene-1,4-diol up to 93% selectivity at 90% conversion of the *cis* analogous. Effects of H_2 partial pressure as well as triethylamine, added phosphine and olefin concentrations on the rate of reaction and on the products distribution were also investigated. The results obtained can be interpreted on the basis of a proposed mechanism in which $RhH(PPh_3)_3$ is the active species. The high selectivity towards *cis-trans* isomerization of *cis*-2-butene-1,4-diol is attributed to steric factors of the Rh(I) coordinated triphenylphosphine groups.

Keywords: Homogeneous catalysis; *Cis–trans* isomerization; Wilkinson catalyst; *Cis*-2-butene-1,4-diol

1. Introduction

Although the Wilkinson complex, $RhCl(PPh_3)_3$, is famous for its applications in hydrogenation processes, analogous studies concerning its use as catalyst precursor for other reactions, such as isomerization, have so far nearly neglected [1–5]. On the contrary, isomerization processes have often been considered a problem on the way to obtain a cleaner hydrogenation.

For several years we have mainly interested in reactions of hydrogen with *cis*-2-butene-1,4-diol, chosen as probe molecule for its versatility to give different products. The following sequence reports the derivatives obtainable in the course of the reaction:



Our research strategy is to tailor a particular heterogeneous or homogeneous catalyst in order to address, with high selectivity, the reaction towards a desired product. In this context, use of the Wilkinson catalyst, directly or as

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doi:10.1016/j.cattod.2004.10.031

precursor, may play an important role in obtaining isomerization derivatives, making advantage eventually of both electronic and/or steric properties [1]. Incidentally, we recall that generally homogeneous catalysts fit better than the heterogeneous analogous in affording selectively a given product.

In this work we report a detailed study on the system $RhCl(PPh_3)_3$–triethylamine in ethanol at 303 K with the purpose to obtain, in hydrogenation conditions, isomerization products. In this regard we aimed at:

(a) having a molecular insight on the intermediates involved in the catalytic process;
(b) getting, with high selectivity, isomerization products difficult to obtain in heterogeneous conditions.

2. Experimental

2.1. Materials

$RhCl(PPh_3)_3$ was prepared according to the literature [1]. *Cis*-2-butene-1,4-diol (Aldrich, purity 95%), ethanol (Fluka, 99.8% analytical grade), tetradecane (Fluka, purity >99%), triphenylphosphine (Aldrich, purity 99%) were used as commercially supplied, without further purification. Triethylamine, NEt_3 (Aldrich, purity 99.5%), was distilled before use. Ultra high purity hydrogen and nitrogen (Multigas >99.9%) were used directly from cylinders.

2.2. Reaction procedure

The hydrogenation of *cis*-2-butene-1,4-diol was carried out in liquid phase at 303 K and at partial pressure of hydrogen between 0.01–0.1 MPa, using ethanol as solvent in a five-necked flask of 100 ml, equipped with a reflux condenser and a thermocouple. Nitrogen was used, when necessary, to balance the total reaction pressure at 0.1 MPa. The reaction temperature was maintained at the constant value ($\pm 0.5\ ^\circ C$) by circulation of silicone oil in an external jacket connected with a thermostat. Stirring was performed with a stirrer head having a permanent magnetic coupling and a stirring rate of 500 rpm was used. The experimental set-up was thoroughly purged with nitrogen before the beginning of the reaction. Then, the rhodium complex (1.08×10^{-5} mol) was dissolved under stirring in the solvent used (25 ml) in atmosphere of H_2 at 303 K, giving a pale yellow solution. Afterwards, NEt_3 was added in the molar ratio $RhCl(PPh_3)_3/NEt_3$ 1:100, the colour of the solution became orange and the system was allowed to equilibrate for one hour. Then 15 ml of a 0.6 M solution of *cis*-2-butene-1,4-diol in ethanol, containing tetradecane as internal standard, was added through one arm of the flask. The orange colour fades to pale yellow when the olefinic compound is added. The progress of the reaction was followed by analysing a sufficient number of samples withdrawn from the reaction mixture. Products analysis was performed with a gas chromatograph (Agilent Technologies model 6890N) equipped with a flame ionization detector. The products separation was obtained by a capillary column (J&W DB-Waxetr, 50 m, i.d. = 0.32 mm). Quantitative analyses were carried out by calculating the area of the chromatographic peaks with an electronic integrator.

The conductivity determination was carried out by using a WTW conductivity meter (model MultiLab 540) with WTW cell (model TetraCon 325), having a cell constant of $0.481\ cm^{-1} \pm 0.5\%$.

3. Results

Reaction of *cis*-2-butene-1,4-diol with hydrogen was carried out in the presence of $RhCl(PPh_3)_3$ and NEt_3 at

Table 1
Hydrogenation and isomerization of *cis*-2-butene-1,4-diol catalysed by $RhCl(PPh_3)_3$ ($\sim 3 \times 10^{-4}$ M) in presence of NEt_3 at 303 K, using ethanol as solvent

P_{H2}(Mpa)	$[NEt_3]$(M)	$[PPh_3]$(M)	[Substrate](M)	k_{obs}(min^{-1})	*Trans*-2-butene-1,4-diol	Selectivity (%)[a] 2-hydroxy tetrahydrofuran	Butane-1,4-diol
0.1	0.005	–	0.2250	1.98	38.42	14.26	47.05
0.1	0.008	–	0.2250	2.34	70.00	13.55	16.15
0.1	0.012	–	0.2250	3.00	74.23	8.31	17.29
0.1	0.016	–	0.2250	3.56	77.45	9.43	12.87
0.1	0.020	–	0.2250	3.81	82.59	8.93	8.15
0.1	0.030	–	0.2250	3.84	79.66	10.69	9.32
0.08	0.030	–	0.2250	3.26	73.10	16.72	9.68
0.05	0.030	–	0.2250	5.36	88.78	5.54	5.46
0.02	0.030	–	0.2250	6.78	95.13	2.43	2.28
0.01	0.030	–	0.2250	8.26	93.46	4.16	2.13
0.01	0.030	0.0006	0.2250	6.18	70.67	13.33	14.41
0.1	0.030	0.0006	0.2250	8.36	88.66	6.04	5.09
0.1	0.030	0.0016	0.2250	9.70	68.28	13.91	16.72
0.1	0.030	–	0.30	1.57	58.86	16.46	23.93
0.1	0.030	–	0.1125	1.44	80.82	7.54	11.64
0.1	0.030	–	0.0563	0.58	31.24	25.75	43.01

[a] The selectivity is calculated at 90% conversion of *cis*-2-butene-1,4-diol.

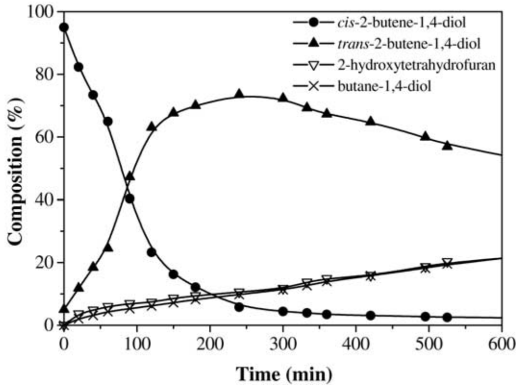


Fig. 1. Composition–time profile relative to hydrogenation and isomerization reaction of *cis*-2-butene-1,4-diol in ethanol at 303 K. Reaction conditions: $[RhCl(PPh_3)_3] = 3 \times 10^{-4}$ M; $[NEt_3] = 3 \times 10^{-2}$ M; $P_{H2} = 0.1$ MPa.

303 K and at 0.1–0.01 MPa partial hydrogen pressure, using ethanol as solvent. Under the experimental conditions used, the reaction proceeds in two steps. The first one leads, with a selectivity ranging from 80% at 0.1 MPa to 93% at 0.01 MPa of H_2, to *trans*-2-butene-1,4-diol. In the second stage the *trans* isomer transforms very slowly into butane-1,4-diol and 2-hydroxytetrahydrofuran. However, in the last case it is difficult to obtain any kinetic results, since the Rh(I) complex, after about 1 day, decomposes. 2-Hydroxytetrahydrofuran was identified by GC and GC–MS and is formed by internal ring closure of γ-hydroxybutyraldehyde, in turn obtained by double bond isomerization of *cis* or *trans*-2-butene-1,4-diol [6]. A typical products composition–time plot showing the course of the reaction of *cis*-2-butene-1,4-diol at 303 K and 0.1 MPa hydrogen pressure is reported in Fig. 1.

Conductometric measurements, performed in ethanolic solutions of $RhCl(PPh_3)_3$ (3×10^{-4} M), pretreated for 1 h with hydrogen, and in presence of NEt_3 under N_2 flow, show that an 1:1 electrolyte is formed during the time (final value of $\Lambda_M \cong 40\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 303 K) and indicates that the following equilibria may occur in our reaction conditions:

$$RhCl(PPh_3)_3 + H_2 + solv \rightleftarrows H_2RhCl(PPh_3)_2(solv) + PPh_3 \quad (1)$$

$$H_2RhCl(PPh_3)_2(solv) + NEt_3 + PPh_3 \rightleftarrows RhH(PPh_3)_3 + NEt_3H^+ + Cl^- + solv \quad (2)$$

In our experimental conditions, these equilibria should be shifted towards the right of the second reaction.

All experimental results, obtained in different conditions, concerning the activity and products distribution, relative to the first stage, are reported in Table 1. Rate constants (k_{obs}) are calculated by the ratio of slopes of plot of *cis*-2-butene-1,4-diol concentration versus reaction time and the complex concentration. Fig. 2 shows the effect of the NEt_3 and olefin concentrations as well as the partial H_2 pressure on the rate constants of the reaction at 303 K.

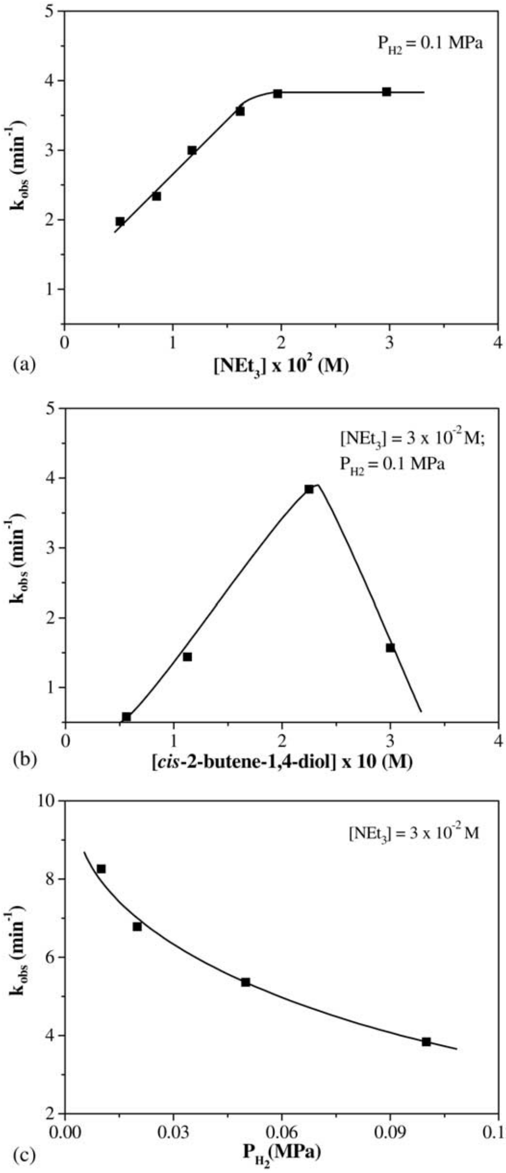
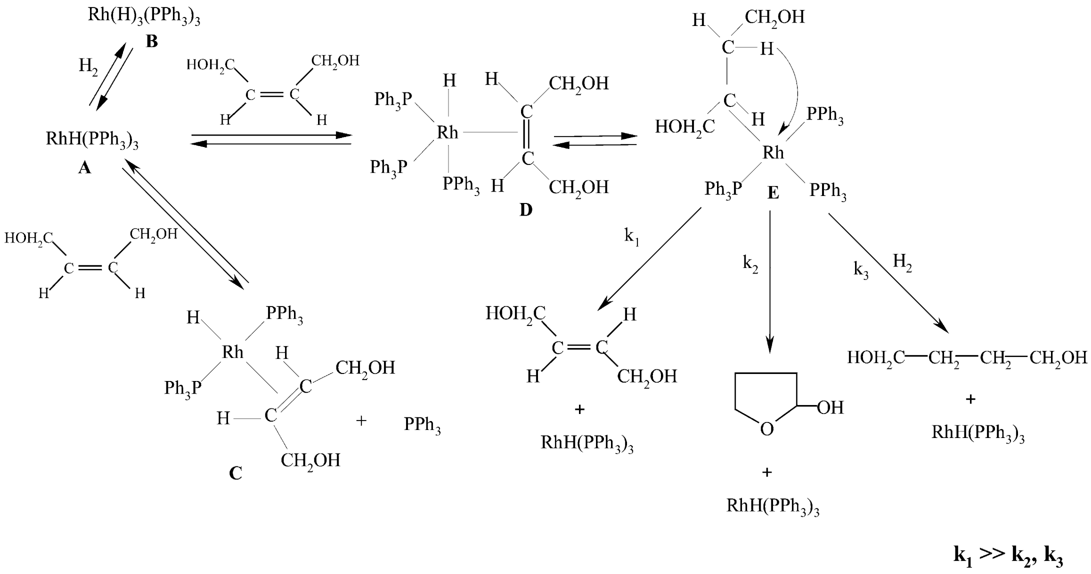


Fig. 2. Dependence of reaction rate constants (k_{obs}) on: (a) the concentration of NEt_3, (b) the olefin concentration and (c) the partial H_2 pressure at 303 K and with 3×10^{-4} M $RhCl(PPh_3)_3$.

4. Discussion

Plot in Fig. 1 and data in Table 1 show that the first stage of the reaction studied involves only conversion of *cis*-2-butene-1,4-diol. The reaction of the analogous geometric *trans* derivative occurs slower in a second stage, when the *cis* concentration is drastically reduced. Rate constants reported in Table 1 and in Fig. 2 show some interesting features:

(a) Rate constants increase as NEt_3 concentration increases, reaching a plateau at higher values of amine concentration (Fig. 2a).
(b) Rate constants increase as olefin concentration increases. However, at higher concentration a decrease of the rate is observed (Fig. 2b).



Scheme 1. Reaction mechanism concerning the hydrogenation and isomerization of *cis*-2-butene-1,4-diol by using $RhCl(PPh_3)_3$ and NEt_3, in ethanol.

(c) Rate constants increase as P_{H2} decreases (Fig. 2c).
(d) Rate constants increase when the phosphine concentration increases (Table 1).

Although the complexity of the reaction does not allow quantitative calculations, we can infer a possible mechanism, accounting for features a–d above reported (Scheme 1).

It is very well known that dihydride Rh(III) species undergo acidic dissociation [7]. On this basis equilibria (1) and (2) are supported not only by our conductometric data but also by literature references [8,9]. Therefore, the square planar $RhH(PPh_3)_3$ is to be considered the main species in our solution and its formation increases, reaching a plateau, as $[NEt_3]$ increases (see Fig. 2(a). On the other hand, observations (b) and (d) suggest that species C is in equilibrium with A and is also kinetically inactive, since H^- and olefin are mutually in *trans* position, leaching of the necessary proximity to undergo hydride migration on the olefinic carbon. This proposed structure stems from H^- having a higher *trans* effect than phosphine [10]. Plot of Fig. 2c shows also that rate constants increase as P_{H2} decreases. Although we have not any spectroscopic evidence, it is possible to suggest that the presence of the inactive species B is the best way to explain the observed dependence. On this regard we recall that analogous Ir(III) trihydrides are well known, whereas Rh(III) trihydrido-species were also postulated at high H_2 pressure [11,12]. Finally, formation of organic products, according to selectivity distribution of Table 1, follows the classical chemical pathway from A, through D and E species, to final products. $RhH(PPh_3)_3$ is formed and re-enters the catalytic cycle. On this basis the marked versatility of E to give *cis*–*trans* isomerization in principle can be attributed to the large hindrance of coordinated phosphines, thus limiting β-H elimination from CH_2OH moiety and favouring, on the same time, hydrogen abstraction from the opposite carbon as indicated in Scheme 1. Thus we afford the more thermodynamically stable *trans* derivative. Therefore, on a kinetic basis, we have $k_1 >> k_2$, k_3 (Scheme 1).

Furthermore, it is noteworthy to highlight the high selectivity to *trans*-2-butene-1,4-diol at 90% conversion of the *cis* analogous (~93% at 0.01 MPa of H_2 pressure), never found in heterogeneous catalysis conditions. So far synthesis of *trans*-2-butene-1,4-diol has been performed by hydrogenation of 2-butyne-1,4-diol with lithium aluminum hydride or diisobutylaluminum hydride [13]. Since the geometric *trans* derivative is an useful starting material for production of different chemicals, catalytic isomerization of *cis*-2-butene-1,4-diol in presence of $RhCl(PPh_3)_3$ and triethylamine can be regarded as an interesting route to its preparation for both the high yield obtainable and the mild reaction conditions used.

5. Conclusions

Wilkinson catalyst in presence of triethylamine proved to be more selective towards the geometric isomerization product than heterogeneous catalysts in the reaction of *cis*-2-butene-1,4-diol with hydrogen at 303 K and at 0.1 MPa partial H_2 pressure. The experimental data concerning the activity and the products distribution, obtained by varying the triethylamine, the added phosphine and the olefin concentrations as well as H_2 partial pressure can be explained on the basis of a mechanism where the $RhH(PPh_3)_3$ is the active species. Furthermore, the mechanistic study indicates that the high selectivity to *trans*-2-butene-1,4-diol can be attributed to the steric hindrance of coordinated phosphines.

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