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ACID-DEPENDENT SELECTIVITY IN THE HOMOGENEOUS HYDROGENATION OF MONO- AND DI-ENES BY ACETATOTRIPHENYLPHOSPHINE COMPLEXES OF RUTHENIUM AND RHODIUM

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Summary

A study has been made of the hydrogenation of mono- and di-enes by catalysts derived from protonation of $Ru(CO_2Me)_2(PPh_3)_2$ and $Rh(CO_2Me)(PPh_3)_3$ in methanolic solution with *p*-toluenesulphonic acid. The rate of hydrogenation is highly dependent on the acidity. Rapid highly selective reduction of cyclic dienes to monoenes occurs. This selectivity is attributed principally to the superior coordinating power of dienes compared with monoenes.

Introduction

It has been shown that the protonation in methanolic solution of carboxylate complexes of ruthenium and rhodium by a strong acid having a non-coordination anion leads, in the presence of triphenylphosphine, to efficient catalysts for the homogeneous hydrogenation of alkenes [1]. The production of catalysts of the type $[Ru(PPh_3)_n]^{2+}$, (n = 2, 3) from $Ru_3O(CO_2Me)_6(PPh_3)_3$, $RuH(CO_2Me)(PPh_3)_3$ and related complexes has also been reported [2]. These studies were carried out mainly at constant acid concentration, but it was noted that the hydrogenation of 1-hexene was acid dependent [2]. There is little published work on selective hydrogenation of dienes under mild conditions. Wilkinson et al. [3] studied the reduction of 1,4- and 1,5-hexadienes by $RuH(Cl)(PPh_3)_3$, and the hydrogenation of 1,5-cyclooctadiene to cyclooctene has also been reported [4], as has the reduction of polycyclic compounds [5]. Ugo et al. reported the hydrogenation of a series of 1,3-dienes, but the use of high temperatures and pressures was necessary [6]. In view of the general interest in selective hydrogenation, the effect of acidity on the reduction of a series of mono- and di-enes in methanol has been studied.

Results

As catalyst precursors the complexes $Ru(CO_2Me)_2(PPh_3)_2$ (I) and $Rh(CO_2Me)(PPh_3)_3$ (II) were used. Reduction of 1-hexene by the protonated ruthenium complex in methanol has been briefly reported [2], and the (unprotonated) rhodium complex has been investigated in benzene solution [7], but no study of the acid-dependence of catalysis by either complex has been made. Because of the greater solubility of the protonated species, *p*-toluenesulphonic acid was used as protonating acid, in place of the previously used fluoroboric acid. The behaviour of the complexes in benzene was studied for comparison. All hydrogenations were at 40°C and less than one atmosphere of hydrogen pressure.

The rate of hydrogenation of 1-hexene as a function of acid concentration is given in Table 1. The constant rate of hydrogenation above acid ratios (i.e. H^+/CO_2Me^-) of ca. 4 for I and 2 for II are attributed to complete loss of the acetate ligands by protonation. In support of this, cations of the type $[Ru(PPh_3)_3](CF_3SO_3)_2$ have been isolated from analogous ruthenium systems [2], and by concentration of solutions of II in methanol at acid ratio 10 using fluoroboric acid as protonating agent, we have obtained the known complex $[Rh(PPh_3)_3](BF_4)$ [7].

The peak in the rate for I at an acid ratio of 0.5 almost certainly arises from the presence of the species $[Ru(CO_2Me)(PPh_3)_2]^+$, but we were unable to isolate a salt of this ion. From the data of Table 1, other alkenes were studied at acid ratios of 0, 0.5 and 10 for complex I and 0 and 10 for complex II. In addition to hydrogenation, appreciable isomerisation of 1-hexene also occurs (Table 2). The protonated solutions , which produce the highest rates of hydrogenation, produce the least isomerisation. .

As a preliminary to investigation of the reduction of dienes, a series of monoenes were investigated (Table 3). With the exception of *trans*-2-hexene,

TABLE 1

ACID-DEPENDENCE OF THE HYDROGENATION OF 1-HEXENE IN METHANOL

Complex, 10^{-3} *M*; 1-hexene, 1*M*; solvent, 50 ml; hydrogen pressure, 400 Torr; *p*-toluenesulphonic acid; 40°C

H^+/CO_2Me^-	Rate (ml/min)	
	$Ru(CO_2Me)_2(PPh_3)_2$	$Rh(CO_2Me)(PPh_3)_3$
0	2.6	9.6
0.25	12.6	
0.5	19.4	14.8
0.75	11.6	
1	10.2	15.9
2	9.7	18.3
4	8.0	18.2
6	7.9	18.1
8	7.7	18.1
10	7.6	18.3
12	7.9	18.1
20	8.1	18.2

TABLE 2

ISOMERISATION DURING HYDROGENATION OF 1-HEXENE

Complex, 10^{-3} *M*; 1-hexene, 1*M*; solvent, 50 ml, hydrogen pressure 350-450 Torr; *p*-toluenesulphonic acid, 40°C; I is $Ru(CO_2Me)_2(PPh_3)_2$, II is $Rh(CO_2Me)(PPh_3)_3$; reaction time 60 min

Complex	Solvent	H^+/CO_2Me^-	Hexane	1-Hexene	*trans*-2-Hexene	*cis*-2-Hexene
I	methanol	0	9.1	52.7	10.1	28.1
I	methanol	0.5	42.1	37.1	13.5	7.3
I	methanol	10	36.2	50.0	9.4	4.4
I	benzene	0	9.9	87.7	1.9	0.5
II	methanol	0	30.1	13.7	38.4	17.0 [a]
II	methanol	10	54.3	32.7	8.0	5.0
II	benzene	0	24.4	40.4	20.6	14.6

[a] 3-Hexenes present (0.8%); compositions are given as mole %.

all were hydrogenated under at least one set of conditions. Both complexes show marked selectivity for 1-alkenes, this effect being most noticeable in benzene solution. For substrates other than terminal linear alkenes, the rate varies on protonation in essentially the same manner as with 1-hexene. The wide variation of rate with acidity indicates that selective reduction of monoenes may be achieved.

In favourable cases, selective reduction of either of two species may be effected by appropriate choice of complex and acidity (cf. cyclohexene and cyclooctene). Data on the reduction of dienes and 1-hexyne are given in Table 4. The variation of rate with acidity is in general similar to that observed with 1-hexene, but the variation in rates is much greater. Of particular significance is the selectivity for reduction to the corresponding monoene (Table 5). This is

TABLE 3

RATES OF HYDROGENATION OF MONOENES (ml/min)

Complex, 10^{-3} *M*; alkene, 1 *M*; solvent, 50 ml; hydrogen pressure 400 Torr; *p*-toluenesulphonic acid, 40°C

Alkene	$Ru(CO_2Me)_2(PPh_3)_2$				$Rh(CO_2Me)(PPh_3)_3$		
	benzene	methanol H^+/CO_2Me^-			benzene	methanol H^+/CO_2Me^-	
		0	0.5	10		0	10
1-Hexene	3.4	2.6	19.4	7.6	3.1	9.6	18.3
1-Octene	9.9	5.9	26.3	12.0	2.9	7.6	10.1
1-Decene	9.2	5.3	31.2	11.3	3.3	8.0	17.7
cis-2-Hexene	0	0	0	0	0	0	4.4
trans-2-Hexene	0	0	0	0	0	0	0
Cyclohexene	0.7	0.2	0.8	0	0	0.4	2.8
Cyclooctene	0	0.8	12.3	4.7	0	0	1.1
2-Methyl-1-pentene	0	2.5	0	0	0	0.9	5.3
2-Ethyl-1-hexene	0	0	0	0	0	1.1	2.8

TABLE 4

RATES OF HYDROGENATION OF DIENES AND 1-HEXYNE (ml/min)

Complex, 10^{-3} *M*; alkene, 1 *M*; solvent, 50 ml; hydrogen pressure, 400 Torr; *p*-toluenesulphonic acid 40°C

Alkene	$Ru(CO_2Me)_2(PPh_3)_2$				$Rh(CO_2Me)(PPh_3)_3$		
	benzene	methanol H^+/CO_2Me^-			benzene	methanol H^+/CO_2Me^-	
		0	0.5	10		0	10
1,5-Cyclooctadiene	0	4.4	77.1	40.7	0	0	0
1,3-Cyclooctadiene	0	0	1.3	1.8	0	1.5	2.2
Bicyclo-(2,2,1)-hepta-2,5-diene	0	3.3	0.5	0	4.4	38.8	84.3
1,4-Cyclohexadiene	0	1.5	4.3	4.6	0	2.0	6.8
1,3-Cyclohexadiene	0	0	0	0	0	21.5	25.4
1,5-Hexadiene	3.6	2.0	37.4	28.9	2.5	34.1	9.7
Limonene	0	0	0	0	0	0.5	4.1
4-Vinylcyclohexene	0	0	15.9	5.8	0	10.4	17.1
1-Hexyne	0	0	0	0	0	18.1	22.9

in general high, and in the case of the symmetrical, cyclic dienes, is in the range of 90-99%. For the non-symmetrical dienes the steric differences between the double bonds play a major role in determining the selectivity, as can be expected from the variation of rate with structure in Table 3. For the symmetrical cyclic dienes, other factors must be involved. In those cases where the diene is reduced at a rate several times that of the corresponding monoene (e.g. 1,5-cyclooctadiene and cyclooctene, 1,3-cyclohexadiene and cyclohexene) the rate difference, coupled with the initial 100% excess of diene is clearly a possible source of the selectivity. However, high selectivity is also observed in the case of 1,3-cyclooctadiene, even though the rate difference for complex I markedly favours cyclooctene reduction. The selectivity here must therefore arise from the superior coordinating ability of the diene, which 'protects' the catalyst from the monoene as long as a significant concentration (which from Table 5 is 1-10% of the total alkene) of the diene is present. This phenomenon, which is merely a manifestation of the chelate effect, must also occur in the reduction of the other cyclic dienes, which are all known to form chelate complexes with ruthenium and rhodium [8], and it is undoubtedly the main cause of the observed selectivity. Attempts to isolate catalyst-diene complexes were not successful. Although in general little change occurred in the pale yellow colours of the solutions during hydrogenation, in two cases marked colour changes occurred on addition and subsequent removal (by hydrogenation) of the diene, supporting the idea of coordination. Thus addition of 1,3-cyclohexadiene to the rhodium complex produced a red-violet colour, which disappeared rapidly as the hydrogen uptake approached that for reduction to cyclohexene, and addition of 1,5-cyclooctadiene to the ruthenium complex produced a colourless solution, which became

TABLE 5

SELECTIVE HYDROGENATION OF DIENES IN METHANOL

Complex, 10^{-3} *M*; alkene, 1 *M*; solvent, 50 ml; hydrogen pressure, 350-450 Torr; *p*-toluenesulphonic acid, 40°C; I is $Ru(CO_2Me)_2(PPh_3)_2$, II is $Rh(CO_2Me)(PPh_3)_3$

Alkene	Complex	H^+/CO_2Me^-	Time (min)	Products (mole %)
1,5-Cyclooctadiene	I	10	60	cyclooctene (91) cyclooctane (9)
1,5-Cyclooctadiene	I	0.5	20	cyclooctene (94) cyclooctane (6)
1,3-Cyclooctadiene	I	10	60	1,3-cyclooctadiene (85) cyclooctene (15)
1,3-Cyclooctadiene	II	10	60	1,3-cyclooctadiene (72) cyclooctene (28)
bicyclo[2,2,1]hepta-2,5-diene	II	10	15	bicyclo[2,2,1]-hepta-2,5-diene (1) bicyclo[2,2,1]-heptene (90) bicyclo[2,2,1]-heptane (9)
1,4-Cyclohexadiene	I	10	60	1,4-cyclohexadiene (81) cyclohexene (19)
1,4-Cyclohexadiene	II	10	60	1,4-cyclohexadiene (64) 1,3-cyclohexadiene (1) cyclohexene (34) cyclohexane (1)
1,3-Cyclohexadiene	II	0	55	cyclohexene (98) cyclohexane (2)
1,3-Cyclohexadiene	II	10	40	cyclohexene (99) cyclohexane (1)
1,5-Hexadiene	I	10	60	1-hexene (76) *cis*-2-hexene (6) *trans*-2-hexene (12) hexane (6)
1,5-Hexadiene	II	0	60	1-hexene (17) *cis*-2-hexene (19) *trans*-2-hexene (47) hexane (17)
Limonene	II	10	60	limonene (34) 4-isopropyl-1-methyl-cyclohexene (66)
4-Vinylcyclohexene	I	0.5	95	4-vinylcyclohexene (52) 4-ethylcyclohexene (23) vinylcyclohexane (22) ethylcyclohexane (3)
4-Vinylcyclohexene	II	10	95	4-vinylcyclohexene (16) 4-ethylcyclohexene (51) vinylcyclohexane (9) ethylcyclohexane (24)
1-Hexyne	II	10	60	1-hexyne (72) 1-hexene (28)

pale yellow again after reduction of the diene. It can be seen from Tables 3 and 4 that, where hydrogenation occurs, the variation of rate with acidity is basically the same for the other alkenes studied as for the terminal linear alkenes. The initial increase in rate with acidity for both complexes could be explained by the enhancement of the degree of coordinative unsaturation on removal of an acetate ligand, which would facilitate alkene coordination and/or hydrogen activation. However, the subsequent reduction in rate for complex I on removal of the second acetate group must be electronic in origin. This, together with the general similarity of the acid dependence for mono- and di-enes of a wide range of steric types, suggests that the electronic effect of acetate removal is more important than steric effects in the alkene and alkyl intermediates in determining the form of the acid-dependence.

Experimental

Microanalyses were performed by the Bernhardt Laboratory, Elbach. GLC analyses used an F and M series 810 chromatograph, using Carbowax 20M, oxydipropionitrile and bis(2-methoxyethyl)adipate columns. Ruthenium and rhodium trichloride trihydrates were obtained from Johnson—Matthey Ltd., alkanes from Fluka, Koch—Light, and Aldrich. $Ru(CO_2Me)_2(PPh_3)_2$ and $Rh(CO_2Me)(PPh_3)_3$ used in this work were prepared by the published methods [2, 7]. A much simplified preparation of the rhodium complex is given below.

Acetatotris(triphenylphosphine)rhodium(I)

Triphenylphosphine (1.18 g, 4.5 mmol) and sodium acetate trihydrate (1.02 g, 7.5 mmol) were stirred in methanol (50 ml) under argon. Rhodium trichloride trihydrate (0.2 g, 0.75 mmol) was added, and the mixture was stirred at room temperature under argon for 2 h. The resulting orange complex was collected, washed with water, methanol, and ether and dried in vacuo. Yield 0.5 g (70%). Analysis: found C, 70.6; H, 5.0; P, 9.4. $C_{56}H_{48}P_3O_2Rh$ calcd.: C, 70.9; H, 5.1; P, 9.8%.

Catalytic studies

The hydrogenation apparatus was similar to that described previously [9]. Alkenes were purified by shaking with their own volume of 10% ferrous sulphate in aqueous 1 *M* sulphuric acid and then with water, filtering through alumina (20 g/100 ml alkene), drying over sodium, and finally distilling from sodium direct into the burette (under argon).

The apparatus was flushed five times with hydrogen before addition of the complex to the solvent. The solution was then stirred 5 min before addition of alkene. All hydrogenations were at 40°C and rates are quoted at 400 Torr of hydrogen pressure, in ml/min corrected to STP. In product studies the hydrogen pressure was maintained in the range 350-450 Torr throughout hydrogenation.

Products were in general identified by gas-chromatographic analysis. The products from the reduction of limonene and 1,5-cyclooctadiene were isolated by fractional distillation and preparative gas-chromatography respectively, and their structures were confirmed by NMR spectroscopy.

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