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Isomerisation of Pentenes with $H_4Ru_4(CO)_{12}$

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*Catalytic isomerisation of 1-pentene to 2-*cis *and 2-*trans*-pentene with $H_4Ru_4(CO)_{12}$ in toluene at 70.4 °C is described. Carbon monoxide, hydrogen, weak acids and polar substances, such as ethyl acetate, decrease the isomerisation rate. Reactions of $H_4Ru_4(CO)_{12}$ with* trans-*$C_2H_2D_2$ and [1,2-D_2] 1-pentene and of $D_4Ru_4(CO)_{12}$ with 1-pentene suggest the operation of a metal–hydride addition–elimination mechanism involving σ-alkyl intermediates. The active species is supposed to be mainly originated by loss of CO to give $H_4Ru_4(CO)_{11}$. Catalytic hydrogenation of the pentene isomers occurs at the approaching of the equilibrium and is largerly enhanced by addition of hydrogen to the reaction system.*

Introduction

Recently we have reported that dodecacarbonyltriruthenium exhibits catalytic properties in the isomerisation of pentenes [1]. Analogous activity is shown by the major products obtained from the reaction between $Ru_3(CO)_{12}$ and the pentene isomers after the equilibrium achievement. Among these compounds $H_4Ru_4(CO)_{12}$ seems to be one of the most active and herein its isomerisation and hydrogenation properties with alkenes are described.

So far reports about the catalytic activity of cluster compounds in the hydrogenation and isomerisation of olefins have principally concerned $Ru_3(CO)_{12}$ [2] and $[Co(CO)_2PR_3]_3$ [3], in presence of H_2, and $Fe_3(CO)_{12}$ [4]. Moreover, $H_4Ru_4(CO)_{12}$ has been reported to hydrogenate cyclohexene and other unsaturated compounds [5].

Experimental

Materials

Tetrahydridododecacarbonyltetraruthenium, *trans*-[D_2]ethylene and [1,2-D_2]1-pentene were prepared by published methods [6–8]. $D_4Ru_4(CO)_{12}$ was prepared by heating at 80 °C for 50 hours $H_4Ru_4(CO)_{12}$, dissolved in toluene, and D_2 at atmosphere pressure in a sealed vial [9]. Toluene was distilled from sodium and stored on molecular sieves. 1-pentene, 2-*cis*-pentene, 2-*trans*-pentene and 2-methyl-1-pentene were Fluka pure grade and were usually used without further purification. Elimination of possible peroxide traces from the pentenes did not give any change in the experimental results.

The value of 5.5 m*M* was determined for the solubility of carbon monoxide in toluene at 70.4 °C and this figure was used to give the concentrations of CO in the reaction systems.

Analyses

Infrared spectra were recorded on a double-beam Beckman IR 4230 spectrophotometer with KBr optics. Proton n.m.r. spectra were determined on a Jeol 60 HL spectrometer and mass spectra on a Hitachi RMU6H mass spectrometer. Gaschromatographic analyses of pentene isomers were performed at 55 °C by a C. Erba Fractovap Model B, using a 4m column of 20% silicon oil 720 on Chromosorb P 60/80 mesh. Gaschromatographic analyses of pentenes and pentane were performed at 25 °C by a C. Erba Fractovap Model M, using a 6m column of 11% $AgNO_3$ and 21% phenylacetonitrile on Chromosorb P 60/80 mesh. In both these analyses helium was used as carrier gas at 50 cc/min. The deuterated pentenes were separated by a C. Erba Fractovap Model P using a 6m, 24mm I. D., column of 25% silicon oil 720 on Chromosorb P 30/60 mesh at 50 °C and helium or nitrogen as carrier gas at 450 cc/min. The various fractions were collected by traps cooled in liquid air.

*Isomerisation of 1-Pentene, 2-*cis*- and 2-*trans*-Pentene*

Required volumes of the catalyst solution at a known concentration were introduced into glass vials equipped with a gc septum and a central bubbling tube. Then the vials were connected to a vacuum line and sealed after saturation with nitrogen. Pentenes and other substances were added by a liquid or gas syringe. The ampoules were placed in a thermostatic tank at 70.4 °C. The extent of the isomerisation reaction was checked by gc analyses and the initial rate determined by the area of the peaks. I.r. spectra of the solution and mass spectra of the gas phase of ampoules, kept in the thermostatic tank several half-

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lifetimes of the isomerisation, showed the formation of $H_2Ru_4(CO)_{13}$ and molecular hydrogen. Moreover gc analysis displayed the presence of pentane, in addition to the pentene isomers.

Isomerisation of [1,2-D_2] 1-Pentene

25.0 mg of $H_4Ru_4(CO)_{12}$ were dissolved with 4.0 ml of toluene in an ampoule, described above, at the reaction temperature. [1,2-D_2] 1-pentene (0.5 ml) was added by a syringe to obtain a molar ratio similar to that used in the kinetic experiments. After suitably long reaction times at 70.4 °C the pentenes were separated by gaschromatography. 1-pentene was pure enough; 2-*cis*- and 2-*trans*-pentene were furtherly separated before running mass and ^1H n.m.r. spectra. The amount and location of deuterium in the deuteriated pentenes were determined by comparing the splitting pattern and the intensity of the resonance signals with those of standard solutions of the corresponding non-deuteriated isomers.

Isomerisation and Redistribution of Deuterium in trans-*D_2 Ethylene*

The ampoules, containing measured volumes of 0.37 m*M* toluene solutions of $H_4Ru_4(CO)_{12}$ were connected to a simple vacuum line and saturated with nitrogen. Then known amounts of *trans*-$C_2H_2D_2$ were condensed in the ampoules. After sealing, they were placed in a thermostatic tank at 70.4 °C. At various times the ampoules were removed and i.r. and mass spectra of the gas phase and the recovered catalyst were recorded.

Results and Discussion

The initial rate values of 1-pentene, 2-*cis*- and 2-*trans*-pentene isomerisation with $H_4Ru_4(CO)_{12}$ at 70.4 °C under different experimental conditions are collected in Table I. The values are expressed as percentage extent of the starting pentene which has been converted to its isomers. A comparison with the corresponding data reported for $Ru_3(CO)_{12}$ [1] shows the higher activity of the hydridocomplex. The initial conversion rate of 1-pentene is proportional to the $H_4Ru_4(CO)_{12}$ concentration and is largely decreased with increasing carbon monoxide partial pressure. Very low CO concentrations are enough to reduce strongly the isomerisation process, while higher pressure gives $H_2Ru_4(CO)_{13}$ and $Ru_3(CO)_{12}$ in successive steps. On this basis it seems very likely that the formation of the active site involves the cleavage of ruthenium–carbon bonds to give the active species $H_4Ru_4(CO)_{11}$. Increasing hydrogen partial pressure also reduces the isomerisation rate, but to a lower extent. This may indicate that, in addition to $H_4Ru_4(CO)_{11}$, also the unsaturated $H_2Ru_4(CO)_{12}$ species, albeit present in lower amount, acts as actual active species. Quantitative effect of the 1-pentene concentration on the isomerisation initial rate has not been determined. Increase of the 1-pentene concentration at constant complex concentration gives, in fact, $H_2Ru_4(CO)_{13}$ and tetranuclear complexes [10] in the early stages of reaction, as i.r. and mass spectra show.

Addition of small amounts of organic acids, such as acetic or formic acid, causes a slight decrease in the isomerisation rate. This is in contrast with the large increase observed with $Ru_3(CO)_{12}$ and assigned to the formation of the ionic species $HRu_3(CO)_{12}^+$ [1]. $H_4Ru_4(CO)_{12}$ does not, in fact, give any furtherly protonated species, detectable in the ^1H n.m.r. spectrum, even by action of such strong acids as H_2SO_4. A parallel decrease of the 1-pentene conversion was found in presence of ethyl acetate. These results and

TABLE I. Inital Isomerisation Rate of Pentenes with $H_4Ru_4(CO)_{12}$ at 70.4 °C.[a]

	$H_4Ru_4(CO)_{12}$ m*M*	Alkene[b] m*M*	CO m*M*	H_2 atm	L[c] m*M*	Initial rate % h^{-1}
1	0.37	46				48
2	0.111	46				14.7
3	0.037	46				5.2
4	0.37	46	1.5×10^{-3}			14
5	0.37	46	3.1×10^{-3}			6
6	0.37	46	8.0×10^{-3}			4.7
7	0.37	46		2.0×10^{-3}		13
8	0.37	46		0.8		5
9	0.37	46			125	13.7
10	0.037	46			70	2.8
11	0.37	46			73	23.3
12	0.37	46				64
13	0.37	46				2.7
14	0.37	46				0.62

[a]Solvent: toluene except for reaction 12 (n-octane). [b]Alkene: 1-pentene except for reaction 13 (2-*cis*-pentene) and reaction 14 (2-*trans*-pentene). [c]L is acetic acid for reactions 9 and 10, ethyl acetate for reaction 11.

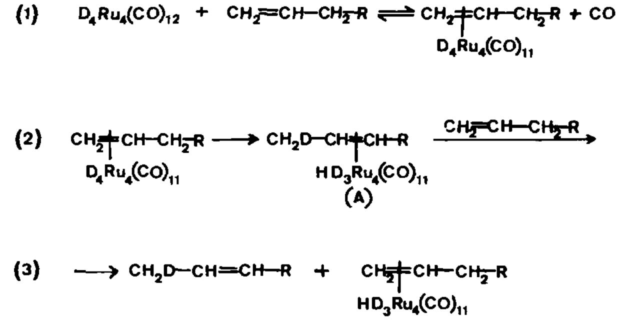
the higher rate measured for n-octane solutions with respect to toluene solutions may be ascribed to a partial competition with the alkene in the coordination on the active site. In all these processes the initial *cis*/*trans* ratio is in the range 0.9–1.0 in toluene and slightly higher in n-octane.

The initial conversion rate of 2-*cis* and 2-*trans*-pentene to their isomers is lower than that of 1-pentene by about an order of magnitude (Table I). Even slower is the isomerisation of 2-methyl-1-pentene. In this case the only isomer formed in the first reaction stages is 2-methyl-2-pentene and no attempt was made to reach the equilibrium composition. These findings are in agreement with previous reports obtained using as catalysts monometalhydridocomplexes [11, 12].

The isomerisation of alkenes catalysed by transition metal complexes is usually considered to proceed by a hydrogen addition–elimination involving σ-alkyl intermediates or by a hydrogen abstraction–addition mechanism involving π-allylic species [4, 13]. Redistribution of the hydrogen isotopes in *trans*-$C_2H_2D_2$ was considered a valid test to demonstrate the operation of an addition–elimination mechanism [14]. When $H_4Ru_4(CO)_{12}$ is reacted with *trans*-$C_2H_2D_2$ in conditions analogous to those used with 1-pentene, C_2H_3D and C_2HD_3 are formed in good amounts. When the concentrations of $H_4Ru_4(CO)_{12}$ and *trans*-$C_2H_2D_2$ are 0.37 m*M* and 65 m*M* respectively, 15% C_2H_3D, 75% $C_2H_2D_2$ and 10% C_2HD_3 are found after 60 minutes at 70.4 °C and 2% C_2H_4, 24.4% C_2H_3D, 54.1% $C_2H_2D_2$, 17.4% C_2HD_3 and 2% C_2D_4 after 105 minutes. Some extent of deuterium is located on the recovered catalyst.

The redistribution process is accompanied by the isomerisation of *trans*-$C_2H_2D_2$ to *cis*-$C_2H_2D_2$, as shown by the absorption band at 844 cm^{-1} in the i.r. spectrum of the final gas phase [15].

$D_4Ru_4(CO)_{12}$ catalyses the double bond migration of 1-pentene at an initial rate very similar to that measured with $H_4Ru_4(CO)_{12}$, but this process is surprisingly not accompanied by substantial transfer of deuterium to the pentene isomers. The mass spectra of the separated pentenes show less than 2.5% monodeuteriated species till 50% conversion of 1-pentene, also when the molar ratio $D_4Ru_4(CO)_{12}$/1-pentene is 1:2. This is analogous to the results obtained in the allylbenzene isomerisation catalysed by $DCo(CO)_4$ [16] and may indicate, if a 1,3 sigmatropic process is to be ruled out, that the isomerisation takes place by the catalytic cycles (2) and (3) such as



$$(1)\quad D_4Ru_4(CO)_{12} + CH_2{=}CH{-}CH_2{-}R \rightleftharpoons \underset{D_4Ru_4(CO)_{11}}{CH_2{=}CH}{-}CH_2{-}R + CO$$

$$(2)\quad \underset{D_4Ru_4(CO)_{11}}{CH_2{=}CH}{-}CH_2{-}R \longrightarrow \underset{\substack{HD_3Ru_4(CO)_{11}\\(A)}}{CH_2D{-}CH{=}CH{-}R} \xrightarrow{CH_2{=}CH{-}CH_2{-}R}$$

$$(3)\quad \longrightarrow CH_2D{-}CH{=}CH{-}R + \underset{HD_3Ru_4(CO)_{11}}{CH_2{=}CH}{-}CH_2{-}R$$

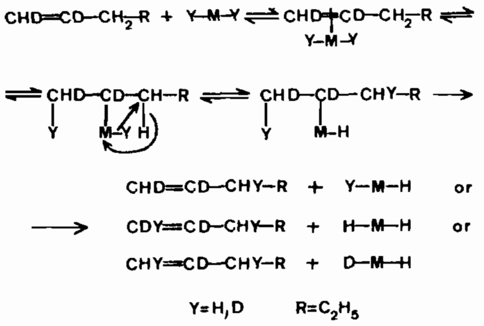
If the active species is displaced from (A) by a free alkene molecule and this isomerisation cycle is much faster than reaction (1), only very few alkene molecules will contain deuterium atoms at least in the first steps of the isomerisation process. The progress of the reaction displays increasing amounts of monodeuteriated pentenes to a statistical distribution. The mass spectrum of the catalyst, recovered at the end of the reaction, shows that the deuterium of $D_4Ru_4(CO)_{12}$ has been partially exchanged. Since, however, the reaction with $D_4Ru_4(CO)_{12}$ does not

TABLE II. Distribution and Location of Deuterium in the Pentene Fractions.[a]

Conversion %		% Distribution						T.D.N[b]	A.D.N. at Each Carbon Atom[c]				
		C_5H_{10}	C_5H_9D	$C_5H_8D_2$	$C_5H_7D_3$	$C_5H_6D_4$	$C_5H_5D_5$		C-1	C-2	C-3	C-4	C-5
0	1-pentene	0.0	0.7	99.0	0.3	0.0	0.0	2.00	0.98	1.02	0.0	0.0	0.0
8	1-pentene	1.4	14.0	73.2	10.8	0.5	0.0	1.95	1.05	0.86	0.04	0.0	0.0
15	1-pentene	3.7	18.8	59.8	17.3	0.5	0.0	1.92	1.08	0.73	0.11	0.0	0.0
33	1-pentene	3.8	23.8	54.7	16.7	1.0	0.5	1.90	1.10	0.65	0.15	0.0	0.0
56	1-pentene	7.0	27.4	43.1	20.7	1.6	0.0	1.82	1.09	0.57	0.16	0.0	0.0
										C-2 + C-3			
33	2-*trans*-	1.6	14.8	60.2	21.0	1.9	0.4	2.08	1.14	0.75		0.07	0.12
56	2-*trans*-	3.7	18.8	43.0	26.9	7.1	0.4	2.16	1.22	0.67		0.10	0.17
56	2-*cis*-	3.4	18.5	43.2	27.8	7.2	0.3	2.19	1.22	0.69		0.10	0.18
81.5	2-*trans*-	7.2	24.3	39.2	21.2	6.9	1.2	2.00	0.91	0.35		0.25	0.49

[a] Experimental conditions are reported in the experimental section. [b] Total deuterium number of each pentene sample. [c] Average deuterium number at each carbon atom; values uncertain to ±0.05.

offer more light on the isomerisation mechanism, we have investigated the conversion of [1,2-D_2]1-pentene with $H_4Ru_4(CO)_{12}$. It takes place by intermolecular transfer of hydrogen and deuterium atoms. Distribution and location of deuterium in the pentenes are shown in Table II. In 1-pentene loss of deuterium from C-2 and accumulation on C-1 and C-3 occur, while no detectable transfer of deuterium on C-4 and C-5 takes place. Variation of the mean deuterium number on C-1 and C-2 is likely to occur by σ-alkyl intermediates, as reported for monohydride complexes [11, 12, 17]. Transfer of deuterium to C-3 can be explained if one suggests an exchange between a hydrogen atom on C-3 and one Y = H, D linked to the Ru_4 cluster in a concerted process involving a cyclic transition state. For clarity reasons, the catalyst is schematically represented by Y–M–Y (Y = H, D) and no account is made of the actual bond situation of the hydrides in $H_4Ru_4(CO)_{12}$.



Beside the Markownikov addition shown above, also the *anti*-Markownikov addition must operate as the loss of deuterium from C-2 of 1-pentene indicates.

After 33% and 56% conversion, 2-*trans*- and 2-*cis*-pentene contain most deuterium at C-1, C-2 and C-3, while little deuterium is present at C-4 and C-5. The presence of deuterium in the ethyl group is likely to be due to a second movement of the double bond and to exchange processes similar to that shown for 1-pentene. With the progress of the reaction a decrease of deuterium at C-1, C-2, C-3 and an increase at C-4 and C-5 can be observed.

The isomerisation of pentenes with $H_4Ru_4(CO)_{12}$ can be therefore interpreted suggesting the operation of σ-alkyl intermediates in a cyclic process and the presence in the catalyst of more than one hydrido ligand explains the occurrence of the hydrogen exchange in the reaction intermediates, as shown above.

Examination of the reaction system containing as starting alkene 1-pentene or 2-*cis*- or 2-*trans*-pentene, at the approaching of the equilibrium between the isomers, shows the presence of little amounts of pentane, molecular hydrogen and $H_2Ru_4(CO)_{13}$, formed by partial dehydrogenation of $H_4Ru_4(CO)_{12}$. The carbon monoxide necessary to give $H_2Ru_4(CO)_{13}$ is likely to come from the reaction of a very small extent of $H_4Ru_4(CO)_{12}$ with the pentene isomers. These facts prevent a true equilibrium between the pentene isomers from being reached, even if after suitably long time periods the extent of the three C_5H_{10} isomers is very near to that obtained with $Ru_3(CO)_{12}$ [1]. With gaseous hydrogen at atmosphere pressure 1-pentene is completely hydrogenated by $H_4Ru_4(CO)_{12}$, but the hydrogenation rate is still lower than the isomerisation rate also under these conditions. The hydrogenation process does take place on the pentene isomers mixture and its occurrence is, at least partially, responsible for the decrease of the isomerisation rate observed in presence of hydrogen.

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