Journal of Organometallic Chemistry, 218 (1981) 115—122
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

HYDROGENATION OF 1,3-BUTADIENES WITH A RHODIUM COMPLEX-LAYERED SILICATE INTERCALATION CATALYST

RASIK RAYTHATHA and THOMAS J. PINNAVAIA

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824 (U.S.A.)

(Received March 6th, 1981)

Summary

$Rh(NBD)(dppe)^+$ (NBD = norbornadiene, dppe = 1,2-bis(diphenylphosphino)ethane) intercalated in hectorite, a swelling layered silicate, catalyzes the overall 1,2 and 1,4 addition of hydrogen to 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene at rates which range from $<10^{-5}$ to 0.83, relative to the homogeneous catalyst. The yields of 1,2 addition products are 1.5 to 2.3 times higher than those obtained under homogeneous reaction conditions. The intercalation effects depend in part on the extent to which the silicate interlayers are swelled by solvent.

Introduction

Amorphous organic polymers and metal oxides have received considerable attention as support matrices for the immobilization of metal complex catalysts, in part, because they possess substantial surface areas and can be readily functionalized to contain almost any desired metal complex [1—6]. The swelling mica type silicates, such as hectorite or montmorillonite, offer an alternative to amorphous matrices for metal complex immobilization [7—9]. These minerals have ordered structures in which silicate layers 9.6 Å thick are separated by layers of hydrated cations [10]. Cationic metal complexes can be electrostatically bonded between the silicate sheets by displacing the alkali metal or alkaline earth ions which normally occupy the interlayer regions. The interlayers can be swelled to various degrees depending in part on the polarity of the swelling solvent, and the nature of the intercalated cation. The swelling ability of the intercalates allows reagent molecules to penetrate the interlayer regions and undergo catalytic reaction at the metal center.

Because of their ordered structures, intercalation catalysts formed with layered silicates have the capability of affecting substrate selectivity based on molecular size. Recent studies of alkyne hydrogenation with intercalated and

0022-328X/82/0000—0000/$02.50

homogeneous rhodium triphenylphosphine complexes have shown that by controlling the degree of swelling, one can favor the reaction of terminal alkynes over spacially more demanding species such as diphenylacetylene by more than a factor of 100 relative to homogeneous solution [7].

The objective of the present study was to examine the effect of intercalation on the properties of $Rh(NBD)(dppe)^+$, NBD = norbornadiene, dppe = 1,2-bis-(diphenylphosphino)ethane, as a catalyst precursor for the overall 1,2 and 1,4 addition of hydrogen to 1,3-butadienes. This reaction system was selected in part because the distribution of monoolefin products is kinetically regulated by the reaction pathways of a common intermediate [11]. Under homogeneous conditions the thermodynamically more stable internal olefin products (1,4 addition) are favored over the synthetically more desirable terminal olefin products (1,2 addition). Thus, it was of interest to determine the effects of catalyst intercalation on product distribution, as well as on the rates of reaction.

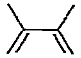
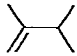
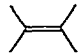
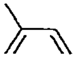
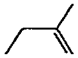
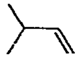
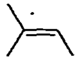
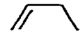
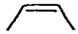
Results

Homogeneous catalyst

Table 1 provides the results for the homogeneous hydrogenation of 1,3-butadiene and two of its methylated derivatives, isoprene and 2,3-dimethyl-1,3-butadiene, in methanol, acetone and benzene with $Rh(NBD)(dppe)^+$ as catalyst precursor. In all cases the yield of monoolefin was essentially quantitative (>98%) and the rate of hydrogen uptake was linear up to 60—80% conversion. The distribution of monoolefins was independent of conversion over the range 10—98%, indicating that the products resulting directly from the overall 1,2

TABLE 1

HOMOGENEOUS HYDROGENATION OF BUTADIENES WITH $Rh(NBD)(dppe)^+$ AS CATALYST PRECURSOR [a]

Diene	Solvent	Diene Conc (*M*)	Diene/Rh	Rate [b]	Products (%) [c]		
							
	Acetone	0.30	280	30	30	70	
	MeOH	0.30	280	58	33	67	
	C_6H_6	0.30	590	1030	33	67	
							
	Acetone	0.50	500	760	13	6	81
	MeOH	0.50	500	1070	14	6	80
	C_6H_6	0.50	500	870	14	7	79
							
	Acetone	0.50	500	780	17	83	
	MeOH	0.30	250	1330	20	80	
	C_6H_6	1.00	1050	1000	19	81	

[a] All reactions were carried out at 25°C and 740 torr. [b] Rates expressed as ml/min/mmol Rh. [c] Product analysis was determined after >98% conversion to monoolefin.

and 1,4 addition of hydrogen to the diene. No alkane formation or isomerization of terminal olefin was observed until all of the diene was consumed. These latter results are consistent with those obtained earlier by Schrock and Osborn [11].

1,3-butadiene and isoprene exhibit high hydrogen uptake rates in each solvent, whereas with 2,3-dimethyl-1,3-butadiene, the rates in methanol and acetone are more than an order of magnitude lower than in benzene. Thus solvation effects can influence reaction rates, at least in the case of the most highly substituted butadiene derivative. Regardless of the effects of solvent on absolute rates of reaction, the product distributions are essentially solvent independent, with the internal olefin products being strongly favored over the terminal olefin.

Intercalation catalyst

Rh(NBD)(dppe)$^+$ was intercalated in hectorite by ion exchange of the perchlorate salt in acetone with the Na$^+$ exchange form of the mineral. A schematic representation of the hectorite structure, which has an idealized unit cell formula of $Na_{0.67}[Mg_{5.33}Li_{0.67}](Si_{8.00})O_{20}(OH,F)_4$, is shown in Fig. 1. Under the exchange conditions employed, approximately 22% of the interlayer Na$^+$ ions were replaced by rhodium complex. Based on estimates of the size of the complex from molecular models (160—200 Å^2), approximately 50—60% of the interlayer surface is occupied by a monolayer of rhodium complex. The remaining area is occupied by solvent and unexchanged Na$^+$. The presence of Rh(NBD)(dppe)$^+$ in the interlayer regions was confirmed by an increase in 001 X-ray spacings from 12.6 Å to 18.4 Å upon replacement of Na$^+$.

Table 2 summarizes the results obtained with the intercalation catalyst under conditions identical to those used to investigate the homogeneous reactions. As

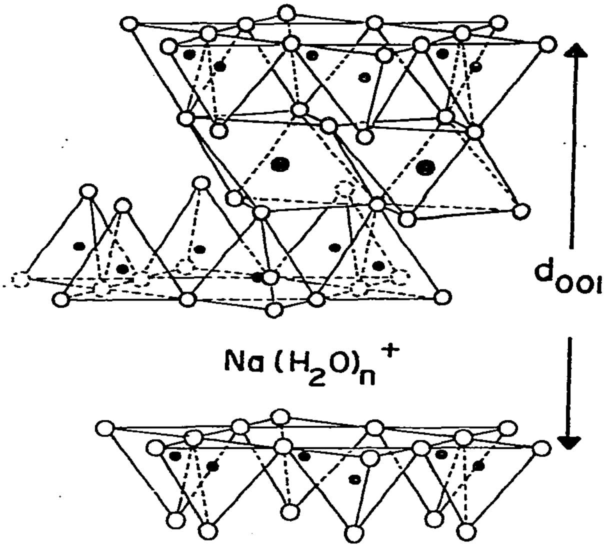
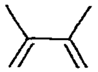
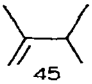
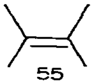
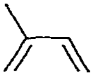
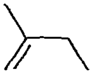
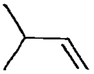
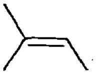
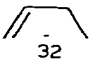


Fig. 1. Schematic representation of Na$^+$-hectorite. Open circles are oxygen atoms. Silicon occupies tetrahedral holes, magnesium and lithium occupy octahedral holes.

TABLE 2

HYDROGENATION OF BUTADIENE WITH Rh(NBD)(dppe)$^+$ INTERCALATED IN HECTORITE [a]

Diene	Solvent	Rate[b]	Products (%)[c]		
					
	Acetone	25		45	55
	MeOH	4.4		60	40
	C_6H_6	< 0.01		—	—
					
	Acetone	300	24	10	66
	MeOH	126	28	16	56
	C_6H_6	<0.01	—	—	—
					
	Acetone	430		32	68
	MeOH	370		39	61
	C_6H_6	<0.01		—	—

[a] Reaction conditions are identical to those described in Table 1 for the analogous homogeneous reactions. [b] ml H_2/min/mmol Rh. [c] Product analysis after >98% conversion.

in the case of the homogeneous reactions, the rates of H_2 uptake were linear up to 60—80% conversion. A 5 min induction period preceded the reduction of 2,3-dimethyl-1,3-butadiene in acetone, and a somewhat longer induction period (~25 min) was observed for this substrate in methanol medium. None of the other substrates showed an induction period with the intercalation catalyst.

A pronounced solvent effect on rates of hydrogenation is observed for each substrate. Essentially no reaction occurs in benzene, even though this solvent gave uniformly high rates for all three substrates under homogeneous conditions. In addition, the intercalated rates are consistently higher in acetone than in methanol, which is the reverse order of solvent activity found under homogeneous conditions.

Except for 2,3-dimethyl-1,3-butadiene reduction in methanol, overall 1,4 addition is favored over 1,2 addition, but the yields of 1,2-addition products are significantly higher for the intercalation catalyst than for the homogeneous catalysts. It is especially noteworthy that the intercalation catalyst provides consistently higher yields of terminal olefins in methanol than in acetone medium. In contrast, the product distributions are virtually identical in these two solvents under homogeneous reaction conditions.

To obtain an indication of the swelling properties of the Rh(NBD)(dppe)$^+$ intercalated hectorite, X-ray powder diffraction measurements were carried out under conditions where the interlayers were solvated by the three solvents used in the catalytic studies. In all cases only one or two orders of 001 reflection were observed, indicating that the interlayers are interstratified. That is, some layers have spacings which are larger or smaller than the value indicated by the first order reflection. Nevertheless, the observed reflections provide a qualitative indication of the extent of interlayer swelling. The positions of the first-order reflections were as follows: 24.5 Å (acetone), 21.5 Å (methanol), 18.4 Å (benzene). Virtually no swelling occurs with benzene, because the same reflection is observed when no solvent occupies the interlayer regions. Both acetone and methanol, however, swell the interlayer region, with the former solvent being the better swelling agent. Substrate may also play a role in the swelling as indicated by the induction periods for 2,3-dimethyl-1,3-butadiene. However, since the induction period is much shorter with acetone than with methanol, the nature of the solvent probably plays the dominant role in determining the extent of swelling.

Discussion

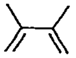
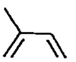
The effects of catalyst intercalation on the hydrogenation of butadienes are best compared relative to homogeneous solution. Relative rates and selectivities toward 1,2 addition are provided in Table 3.

The dramatic differences in relative rates for the three different solvent systems can be related to the extent of interlayer swelling. In the case of benzene, the interlayers are not swollen nor sufficiently mobile to permit ready access to the metal centers by even the smallest substrate and, consequently, the rates are more than 10^5 times lower than in homogeneous solution. However, the relative rates increase greatly when the interlayers are swelled by acetone and methanol beyond the dimensions of the unsolvated intercalate.

The size of the substrate molecule relative to the extent of interlayer swelling seems to play some role in determining the differences in relative rates for the methanol- and acetone-solvated systems. The relative rate for 2,3-dimethyl-1,3-butadiene reduction decreases by a factor of ten upon replacing acetone with the poorer swelling solvent methanol, whereas for 1,3-butadiene the relative rates differ by only a factor of two for these two solvents. Thus the smaller substrate has better accessibility to the metal centers.

TABLE 3

RATES AND SELECTIVITIES TOWARD 1,2 ADDITION PRODUCTS FOR THE INTERCALATED CATALYST, RELATIVE TO THE HOMOGENEOUS CATALYST

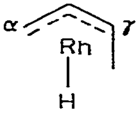
Diene	Solvent	Rel. rate [a]	Rel. selectivity [b]
	Acetone	0.83	1.5
	MeOH	0.08	1.8
	C_6H_6	$<10^{-5}$	—
	Acetone	0.39	1.8
	MeOH	0.12	2.3
	C_6H_6	$<10^{-5}$	—
	Acetone	0.55	1.6
	MeOH	0.28	2.3
	C_6H_6	$<10^{-5}$	—

[a] Intercalated rate/homogeneous rate under reaction conditions described in Tables 1 and 2. [b] Intercalated 1,2 addition products/homogeneous 1,2 addition products.

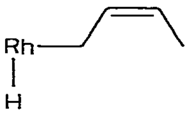
Substrate size, however, is not the only factor influencing relative rates. Although the relative rates increase with decreasing substrate size when the reaction is carried out in methanol solvated interlayers, no correlation exists between size and relative rate when the interlayers are solvated by acetone. It appears that the spacial requirements of the substrate are important when the extent of swelling is more nearly comparable to the size of the substrate (as with methanol) but other effects, such as differences in solvation between the intercalated and homogeneous states, begin to dominate when the swelling is larger and the interlayer adopt more solution-like character. The potential importance of solvation effects under homogeneous reaction conditions is clearly illustrated by the large differences in absolute rates for 2,3-dimethyl-1,3-butadiene reduction (cf. Table 1) in benzene and methanol or acetone.

The effects of catalyst intercalation on monoolefin product distribution, though modest in absolute terms, is significant. Depending on the substrate and solvent, the yields of 1,2 addition products for the intercalation catalyst are 150 to 230% higher than those obtained under homogeneous conditions. The increases in the fraction of terminal olefin products in the case of 2,3-dimethyl-1,3-butadiene are comparable to those induced for this substrate in homogeneous solution when the diphosphine ligand at the rhodium center is replaced by a diarsine ligand [11]. Since the product distribution and homogeneous conditions is remarkably independent of solvent polarity (cf.; Table 1), it is unlikely that changes in solvation under intercalated conditions are responsible for the increased yields of terminal olefins.

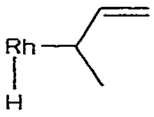
The mechanism of conjugated diene reduction with Rh(NBD)(dppe)$^+$ as the catalyst precursor has been shown to involve a coordinately unsaturated pathway in which the diene adds to the metal center before oxidative addition of hydrogen [11]. Little is known regarding the structure of the RhH(R)(dppe)$^+$ intermediate which precedes the reductive elimination of the olefin, but an η^3-allyl species (I) has been proposed for the homogeneous catalytic reduction of 1,3-dienes [12—14]. The transfer of hydrogen to the α carbon would lead to overall 1,4 addition, whereas overall 1,2 addition would result from hydrogen transfer to the γ position. A facile η^3 to η^1 rearrangement, analogous to that proposed for *syn—anti* interchange of η^3-allyl complexes [15], could precede the hydrogen transfer step. In this latter case, the distribution of monoolefin products would be determined by the relative energies of the η^1 species II and III.



(I)



(II)



(III)

Whatever the precise mechanistic details may be, catalyst intercalation decreases the difference in activation free energy for the two transition states which lead to overall 1,2 and 1,4 addition. For all three substrates investigated, the tendency toward 1,2 addition products is consistently higher for the more constricted methanol-solvated intercalate than for the acetone-solvated intercalate. Whether the effects of catalyst intercalation on the distribution of kinetically regulated products result from spacial factors or from polarization effects induced by the charged silicate sheets cannot be determined at this time. Since the intercalation catalyst is interstratified and not uniformly swollen by acetone or methanol, it is possible that only a fraction of the interlayers have the proper spacing or charge density to influence product distribution. Interstratification in hectorite and other naturally occurring layered silicates results in part from non-uniform charge distribution on the silicate sheets [16]. A layered silicate intercalation catalyst with a more uniform charge distribution may lead to more dramatic effects on product distribution.

Experimental

Materials

Naturally occurring Na^+-hectorite (California) was obtained from the Baroid Division of NL Industries. The sample was used as received in centrifuged spray dried form and with a particle size <2 μm. Chemical exchange of Na^+ in the native mineral with 1.0 *M* $Cu(NO_3)_2$ and subsequent chemical analysis of the mineral for Cu^{2+} indicated the cation exchange capacity to be 70.0 meg/100 g. Rh(NBD)(acac) was obtained by reaction of $[Rh(NBD)Cl]_2$ and acetylacetone according to method of Cramer [17]. The method of Abel et al. [18] was used to prepare $[Rh(NBD)Cl]_2$ from $RhCl_3 \cdot 3\ H_2O$ (Engelhard Industries). 2,3-Dimethyl-1,3-butadiene and isoprene (Chemical Samples Co.) were freshly distilled under an argon atmosphere before use as substrates. Fresh stock solutions of 1,3-butadiene (Pfaltz-Bauer) were prepared by dissolving the gas in the desired solvents and determining the concentration based on the mass increase.

[Rh(NBD)(dppe)]ClO_4. This compound was prepared by reaction of the acetylacetonate complex, Rh(NBD)(acac), with dppe in the presence of $HClO_4$ according to the method of Schrock and Osborn [19]. The proton and phosphorus NMR spectra of the product were in good agreement with the previously reported spectra [19]. ^1H NMR (CD_2Cl_2) 5.34 (4, olefin), 4.33 (2, methine), 1.84 (2, methylene), 2.37 (4, PCH_2CH_2P). ^{31}P NMR (CH_2Cl_2) —55.8 ppm (d, J(Rh—P) = 159 Hz). IR (mull) 1439, 1485 cm^{-1} (C=C). λ_{max} (CH_2Cl_2) = 473 nm.

[Rh(NBD)(dppe)$^+$-hectorite. Na^+-hectorite (100 mg, 0.070 meq) was stirred for 30 min in 5 ml of acetone or methanol and then [Rh(NBD)(dppe)]ClO_4 (18.5 mg, 0.027 meq) in 5 ml of the same solvent was added. Stirring was continued for 10 min and the yellowish orange intercalate was filtered and washed several times with 5-ml portions of solvent to ensure complete removal of unexchanged rhodium complex. Elemental analysis indicated 1.62 wt% Rh. IR (mull) 1439, 1485 cm^{-1} (C=C). λ_{max} (mull) = 465 nm.

Hydrogenation studies

The hydrogenation reactions were carried out in a specially designed flask to minimize creeping of the finally divided intercalation catalyst [8]. The flask was charged with degassed solvent and catalyst and then was attached to a manifold fitted with a mercury manometer and a gas buret with a mercury leveling bulb. The entire assembly was evacuated and purged with dry hydrogen. A one-hour hydrogenation period preceded the injection of substrate into the flask. The hydrogen uptake was monitored at 25°C and a total pressure of 740 Torr. After each run with the intercalation catalyst, the catalyst was filtered off and the clear filtrate was checked for hydrogenation activity to ensure that the observed rates were due only to immobilized catalyst. In all cases no activity could be detected. Product analysis was carried out by gas chromatography. The columns were 10 ft × 1/8 in. 10% UCW-98 (Hewlett-Packard) on 80—100 mesh Chromosorb-W and 15 ft × 1/8 in. 10% $AgNO_3$ in 10% propylene glycol on 80—100 mesh Chromosorb-W.

Physical measurements

X-ray powder diffraction data were obtained by placing thin film samples on glass slides and recording the diffraction patterns on a Philips X-ray diffractometer with Ni-filtered Cu-K_α radiation. Diffraction patterns under different condition of solvation were obtained by allowing the film to equilibrate under the solvent for a few hours, and then keeping the film wetted while in the X-ray beam. UV-visible spectra were recorded on a Varian Associates Cary-17 Spectrophotometer. Spectra of the intercalate were prepared by mulling in mineral oil and placing the mull between silica disks. A mull sample of the native Na^+-hectorite was placed in the reference beam to partially compensate for scattering. Infrared spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer. Spectra in the region 1800—1200 cm^{-1} were obtained by mulling the samples in fluorolube and placing the mulls between CsI disks. ^1H NMR spectra were recorded at 60 MHz on a Varian Associates Model T-60 spectrometer. Proton-decoupled ^{31}P spectra were obtained on a Bruker HFX-90 spectrometer operated at 36.44 MHz. An external 85% H_3PO_4 solution was used as a reference.

Acknowledgement

Partial support of this work through National Science Foundation grant CHE-8002413 is gratefully acknowledged.

References

1 D.D. Whitehorst, Chemtech, 44 (1980).
2 B.C. Gates and J. Lieto, Chemtech, 195 (1980).
3 R.H. Grubbs, Chemtech, 512 (1977).
4 F.R. Hartley and P.N. Vezey, Adv. Organometal. Chem., 15 (1977) 189.
5 Yu.I. Yermakov, Catal. Rev.-Sci. Eng., 13 (1976) 77.
6 J.C. Bailar, Jr., Catal. Rev.-Sci. Eng., 10 (1974) 17.
7 P.K. Welty and T.J. Plinnavaia, J. Amer. Chem. Soc., 97 (1975) 3819.
8 T.J. Pinnavaia, R. Raythatha, J.G.S. Lee, L.J. Halloran and J.F. Hoffman, J. Amer. Chem. Soc., 101 (1979) 6891.
9 W.H. Quayle and T.J. Pinnavaia, Inorg. Chem., 18 (1979) 2840.
10 R.E. Grim, Clay Mineralogy, 2nd ed., McGraw-Hill, New York, 1968, pp. 77—92.
11 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 98 (1976) 4450.
12 B.R. James, Homogeneous Hydrogenation, John Wiley, New York, 1972, pp. 116—123.
13 G.F. Pregaglia, G.F. Ferrari, A. Andreetta, G. Capparella, F. Genoni and R. Ugo, J. Organometal. Chem., 70 (1974) 89.
14 L.Kh. Freidlin, E.F. Litvin and L.F. Topuridze, Zh. Org. Khim., (1972) 669.
15 K. Vrieze in L.M. Jackson and F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1975, pp. 441—488.
16 E. Frey and G. Lagally in M.M. Mortland and V.C. Farmer, Eds., Proc. Intern. Clay Conf., 1978, Elsevier, New York, 1979, p. 131.
17 R. Cramer, J. Amer. Chem. Soc., 86 (1964) 217.
18 E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc., (1959) 3178.
19 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 93 (1971) 2397.