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Rh/AlPO$_4$ Catalysts

IX. Liquid-Phase Hydrogenation and Isomerization of α,β-Unsaturated Alcohols

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The liquid-phase catalytic hydrogenation of several α,β-unsaturated alcohols has been carried out at 293–323 K and in an initial hydrogen pressure range of 0.3–0.7 MPa, on a 1 wt% rhodium catalyst supported on aluminum orthophosphate. Reaction kinetics and solvent effects on the reaction rate were studied. Unlike the hydrogenation of variously substituted olefins with the same catalysts, the selectivity toward α,β-unsaturated alcohols is not due 100% to formation of the corresponding carbonyl compound through isomerization of the double bond in addition to the expected hydrogenated compounds. Furthermore, in the presence of the catalyst the carbonyl compounds react with methanol (employed as a solvent) to form the corresponding 1,1-dimethoxy derivatives. The initial hydrogenation and isomerization rates increase in the order $CH_2{=}CHC(CH_3)_2OH > CH_2{=}CHCH(CH_3)OH > CH_2{=}CHCH_2OH \geq CH_3CH{=}CHCH_2OH > CH_2{=}C(CH_3)CH_2OH$. So, the methyl group promotes a different behavior according to its position. It is activating when the substitution is developed in the hydroxymethyl group, whereas it is deactivating when it is linked to one of the carbons in the olefinic double bond. This behavior is ascribed to the effects of methyl substitution known as hyperconjugation. These effects are also evaluated through several isokinetic parameters obtained from the existence of a linear correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (and between E_a and ln A) known as the "compensation effect." On the basis of these results, and taking into account that the isomerization process was found to occur only when the substrate possesses at least one hydrogen atom in the hydroxymethyl group and when molecular hydrogen is present in the reaction medium, a concerted mechanism through a common transition state is suggested that is capable of evolving into hydrogenation and/or isomerization products. © 1988 Academic Press, Inc.

INTRODUCTION

The influence of olefinic substrate structures on their reactivity is of great interest with respect to the mechanistic study of alkene hydrogenations with supported metal catalysts (*1, 2*). In this regard, we have for a number of years conducted research on the synthesis and characterization of Ni and Rh catalysts supported on aluminum orthophosphates (*3–5*), as well as on their application in different processes aimed to establish the influence of the catalyst and the substrate structure on the adsorptivity of unsaturated compounds and on the reactivity of adsorbed species (*6–11*). Our Rh/AlPO$_4$ systems have enabled us to achieve 100% selectivity in the reduction of the double bond of olefins bearing a variety of organic functions (*9, 10*) with neither C–N nor C–O bond hydrogenolysis nor carbonyl group hydrogenation. Only Allyl alcohol yielded the side reaction product corresponding to the isomerization of the double bond to form propanal.

In recent research (*12*), however, the only products detected in the liquid-phase catalytic hydrogenation of allyl alcohols (2-propen-1-ol, 2-methyl-2-propen-1-ol and 2-buten-1-ol) were the corresponding saturated alcohols, when a series of nickel catalysts at 20 wt% supported on Al$_2$O$_3$, SiO$_2$, and three different types of AlPO$_4$ were employed.

This work was aimed to expand research in this field by studying the liquid-phase hydrogenation and isomerization of vari-

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ously substituted α,β-unsaturated alcohols at low hydrogen pressures and room temperatures in order to determine the influence of supported metal on the reaction mechanism.

EXPERIMENTAL

Catalyst

A catalyst containing 1 wt% rhodium was prepared by impregnation of the support, a powdered aluminum orthophosphate (particle size 0.149 mm) obtained by precipitation with propylene oxide from aqueous solutions of $AlCl_3 \cdot 6H_2O$ and H_3PO_4 (85 wt%). It was impregnated to incipient wetness with aqueous rhodium chloride, oven-dried at 393 K for 24 h, reduced in a hydrogen stream at 473 K for $\frac{1}{2}$ h, and finally cooled to room temperature in the same hydrogen stream. A more detailed description of the synthesis and characterization of both the support and the catalyst was given in earlier papers (*3–8*).

The textural properties of $AlPO_4$, determined from nitrogen adsorption at liquid nitrogen temperature, were as follows: surface area, 228 m^2g^{-1}; pore volume, 0.94 ml g^{-1}; mean pore diameter, 2–4 nm. The metal surface area in the supported rhodium catalyst, determined by TEM (assuming spherical geometry), was 115 $m^2\ g_{Rh}^{-1}$.

The acid–base properties of the catalysts were determined by a spectrophotometric method described elsewhere (*13, 14*), based on the irreversible adsorption of a variety of acid and basic organic compounds. The concentrations of acid sites obtained by titration with cyclohexylamine and pyridine were 531 and 163 μmol g^{-1}, respectively.

Apparatus, Materials, and Procedure

Hydrogenation experiments were carried out according to the procedure described previously (*5–12*), under vigorous shaking in a conventional low-pressure Gerhardt reactor furnished with a manometer whereby the actual pressure in the reaction vessel was read, at temperatures between 293 and 323 K. The reaction temperature was controlled by pumping water from a thermostatic bath through the vessel jacket, with an accuracy of ±0.5 K. Portions of 25 ml of 1 *M* solutions of the substrate in methanol (or another solvent in some reactions) were used at low hydrogen pressures (0.3–0.7 MPa). Initial reaction rates, r_0, were obtained by plotting hydrogen consumption as a function of time, from a least-squares fit to the slopes of the linear portions of pressure decrease.

The chromatographically pure alcohols (2-propen-1-ol, 2-buten-1-ol, 3-buten-2-ol, 2-methyl-2- propen-1-ol and 2-methyl-3-buten-2-ol) were used as supplied commercially after distillation under reduced pressure and low temperature. Then they were passed through active acidic aluminum oxide powder for chromatography (Merck) which was activated at 673 K in flowing ultrapure nitrogen. All solvents were dried and distilled prior to use to remove potential catalytic poisons. Hydrogen (99.999% SEO) was used without further purification.

The reaction products were characterized chromatographically with the aid of a Hewlett–Packard 5830A chromatograph furnished with a flame ionization detector and three different columns packed with 5% polyphenyl ether, 5% 20M-Carbowax, and 5% Squalane, on Chromosorb GAW-DMCS 80/100. The mass spectrometer of a Hewlett–Packard GC-EM (Model 5992 B) was also used for this purpose.

RESULTS AND DISCUSSION

The hydrogenation reactions were carried out under conditions where overall reaction rates were not influenced by diffusion. Thus, the effect of the external diffusion was checked by lowering the shaking regime from 300 to 100 strokes per minute. The hydrogenation rates were independent of the agitation speed above 220 strokes per minute. In addition, to avoid the potential interference of internal diffusion, the catalyst was sieved down to 0.149 mm, thereby excluding the possible influence of hydrogen diffusion on the hydrogenation rate as demonstrated in a previous work (*12*) where the hydrogenation reaction of allyl alcohol on $NI/AlPO_4$ of several grain sizes was carried out under the same experimental conditions used in this work. Internal diffusion control was found to operate when the grain size was greater than 0.21 mm.

Furthermore, the hydrogen uptake rate, r, in the hydrogenation of 2-methyl-3-buten-2-ol was found to be linearly related to the weight of the catalyst used, w. The plot of r^{-1} versus w^{-1} was also linear, and from the inverse of the interception at origin (*15*), a hydrogen transfer rate of 0.87 10^{-3} mol s^{-1} was obtained. Due to the fact that whole reactions exhibit a hydrogen uptake rate 30–50 orders of magnitude lower than this limit, we have to conclude that kinetic data in the range of operating variables are free from transport influences.

Under the present reaction conditions at 293 K, the reaction order in the initial hydrogen pressure determined between 0.3 and 0.7 MPa was 1.4, i.e., much higher than those typically obtained with this catalyst for a number of olefins (*8–11*). The reaction order in the substrate concentration, determined from concentrations in the range 0.5–3 *M*, was found to be −0.5, which was lower than the zero order obtained for other substrates when the same catalyst was used (*8–11*).

The negative reaction order in the olefin concentration could be accounted for by the very strong adsorption of the carbonyl group, produced in the isomerization reaction, on the catalyst surface which would be thoroughly covered, thus hindering the access of olefin to the catalyst's active sites. Also, the higher the hydrogen pressure is, the greater the possibility of hydrogen filtering through the olefin molecules and reaching the catalyst surface, as shown in the relatively high reaction order in the pressure. So, the hydrogenation rate could be assumed to be proportional to the rate at which hydrogen reaches available active sites. However, the hydrogenation rate, alternatively, could also be proportional to the number of surface metal atoms able to act as active sites and increase with hydrogen pressure.

On the other hand, there are a number of papers in the literature (*16–19*) evaluating the effect of the solvent on the hydrogenation process, all of which arrive at a relationship similar to that reported by Drougard and Decroocq (*19*):

$$\log(r_D/r_M) = \lambda'\tau' \qquad (1)$$

In our case r_D is the initial hydrogenation rate of 2-methyl-3-buten-2-ol in solvent D, r_M is the initial hydrogenation rate in a standard solvent (methanol), and λ' is a parameter accounting for the sensitivity of the hydrogenation rate to solvent changes. Constant τ', typical of each solvent, is determined from the expression proposed by Cerveny *et al.* (*20*) for a given catalyst using cyclohexene as the standard substrate:

$$\tau' = \log(r_D^c/r_M^c) \qquad (2)$$

Here r_D^c and r_M^c are the initial rates of cyclohexene hydrogenation in solvent D and in methanol, respectively. In this connection $\lambda' = 1$ for the cyclohexene hydrogenation using methanol as the solvent.

Table 1 lists the initial hydrogenation rates of cyclohexene and 2-methyl-3-buten-2-ol obtained by using the $Rh/AlPO_4$ catalysts and different solvents, as well as the τ' value of each solvent, as calculated from Eq. (2).

By plotting the data listed in Table 1, in the form of $\log(r_D/r_M)$ as a function of τ', a straight line with slope $\lambda' = 0.814$ was obtained with a correlation coefficient of 0.99. This is indicative of the accuracy of the τ' values used, despite their lack of universality since they are different for each catalyst.

Thus, the sensitivity to solvent changes shown by the 1% $Rh/AlPO_4$ catalyst used herein in the hydrogenation of 2-methyl-3-buten-2-ol must be similar to that of the

TABLE 1

Initial Hydrogenation Rates, r_0, of Cyclohexene, 2-Methyl-3-buten-2-ol, and Styrene with Rh/AlPO$_4$ at 0.55 MPa and 293 K in Different Solvents and Their Respective τ' Constants and Dielectric Constants, ε

Solvent	r_0 (mol s^{-1} g^{-1}) × 10^3			τ'	ε (D)
	Cyclohexene	2-Methyl-3-buten-2-ol	Styrene		
Methanol	52.2	31.7	11.7	0.00	32.6
Ethanol	25.2	17.0	7.3	−0.32	24.3
1-Propanol	12.7	9.3	6.0	−0.62	20.1
2-Propanol	10.8	8.3	4.2	−0.68	18.3
Cyclohexane	9.0	7.5	—	−0.76	2.0

catalyst consisting of 5% Pt on silica gel used by Cerveny *et al.* (*20*) ($\lambda' = 0.86$), and different from that consisting of 5% Pt supported on active charcoal, also used by this author (*20*) ($\lambda' = 0.54$).

It is also of interest to determine the sensitivity of the reactant structures to the solvent effects by comparing the λ' values obtained for the same catalyst with different substrates. Thus, from values previously obtained for styrene hydrogenation (*8*), and also collected in Table 1, a straight line of slope $\lambda' = 0.55$ is obtained by using Eq. (1). These results are contrary to those described by Cerveny and Ruzicka (*2*) according to which the highest sensitivity to the change in the solvent was observed in substrates containing the benzene ring, since the sensitivity of the reaction rate to the solvent change decreases on going from cyclohexene ($\lambda' = 1$) to 2-methyl-3-buten-2-ol ($\lambda' = 0.814$) and styrene ($\lambda' = 0.55$). The linear correlation ($r \geq 0.99$ in the three cases) between the logarithm of the hydrogenation rates and the dielectric constants, ε, of the alcohol used (Fig. 1) also accounts for the same conclusion, considering the decreasing values of slopes: 48.6×10^{-3}, 41.5×10^{-3}, and 30.0×10^{-3}, for cyclohexene, 2-methyl-3-buten-2-ol, and styrene, respectively.

Such behavior seems to demonstrate that the protic character of alcohols plays an important role due to its ability to accommodate a separation of charge in the transition state. However, the relative lack of sensitivity to solvent polarity is also noteworthy when compared with processes developed through a zwitterionic mechanism (*21*).

Earlier experiments involving the hydrogenation of numerous olefins bearing different organic functions (*9*) showed that the selectivity of hydrogenation over side reactions when using Rh/AlPO$_4$ as the catalyst was 100% in every case, except in α,β-unsaturated alcohols. Thus, the hydrogenation of *E*-3-phenyl-2-propen-1-ol was accompanied by isomerization of the C–C double bond to 3-phenylpropanal and by a

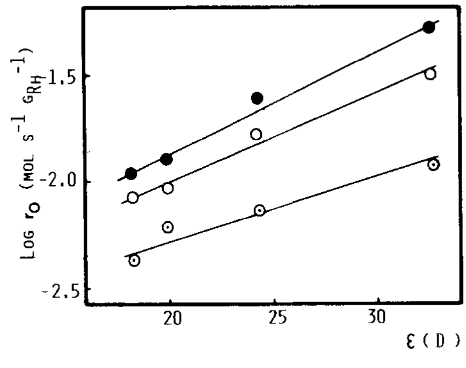

FIG. 1. Influence of dielectric constant, ε, of different solvents on the catalytic activity, r_0, of Rh/AlPO$_4$ catalyst in the hydrogenation of cyclohexane (●), 2-methyl-3-buten-2-ol (○), and styrene (⊙) at 0.55 MPa and 293 K.

TABLE 2

Reaction Times, Percentages Conversion, and Initial Rates of Formation, r, for 1,1-Dimethoxy Derivatives of the Different Carbonyl Compounds

Substrate	Time (min)	Conversion (%)	$r \times 10^3$ (mol s^{-1} g_{Rh}^{-1})
Propanal	75	100	10.0
Methylpropanal	260	100	25.0
Butanal	210	100	40.0
Butanone	15–150	10	0.2

side hydrogenolysis yielding 1-phenyl-1-propene and *n*-propylbenzene (*10*). Similarly, in the hydrogenation of allyl alcohols, the subject matter of this paper, the process was accompanied by isomerization of the olefinic double bond to the corresponding aldehyde or ketone. No hydrogenolysis product was found.

When methanol was used as the solvent, the occurrence of aldehydes or ketones in the reaction medium gave rise to acetals or ketals, respectively, in the presence of the catalyst. To carry out a deeper analysis of the hydrogenation and isomerization of allyl alcohols, we studied the formation of the 1,1-dimethoxy derivatives of different carbonyl compounds yielded upon isomerization of the allyl alcohols, namely, propanal, methylpropanal, butanal, and butanone. The experiments, carried out under the same experimental conditions as the hydrogenation reaction, but in the absence of hydrogen (the reaction vessel containing 25 ml of 1 *M* solution of the carbonyl compound in methanol at 293 K in the presence of 0.2 g of catalyst), yielded the reaction profiles given in Fig. 2, from which the initial formation rates, r, were obtained. Their corresponding values are shown in Table 2. Blank tests carried out in the absence of the catalyst revealed the absence of acetals and ketals.

Propanal, methylpropanal, and butanal were 100% converted to their 1,1-dimethoxy derivatives, whereas the butanone reached only 10% conversion, which was attained after 15 min and kept constant after 150 min. The initial formation rates of the acetals from the aldehydes were in the sequence butanal > methylpropanal > propanal, whereas that of butanone was much lower. This behavior may be explained taking into account that the carbonyl group in ketones exhibits a lower electrophilic character than in aldehydes and also that there is a steric effect of the methyl group in butanone hindering the attack of methanol on the carbonyl group which is not present in the aldehydes. This behavior is similar to that obtained (*22*) in the acetalization of aldehydes by ethylene glycol in the presence of ketones due to the effects of Al_2O_3 or SiO_2, which are described as effective and convenient catalysts for the selective protection of the formyl group of ketoaldehydes.

Consequently, in dealing with the hydrogenation and isomerization of allyl alcohols on $Rh/AlPO_4$ catalysts, we ought to consider both the carbonyl compound and its 1,1-dimethoxy derivatives as isomerization products, because the concentration ratio between the two, determined chromatographically, depends on the time elapsed between the formation of the carbonyl compound and its analysis. So, if the reaction mixture is allowed to stand long enough,

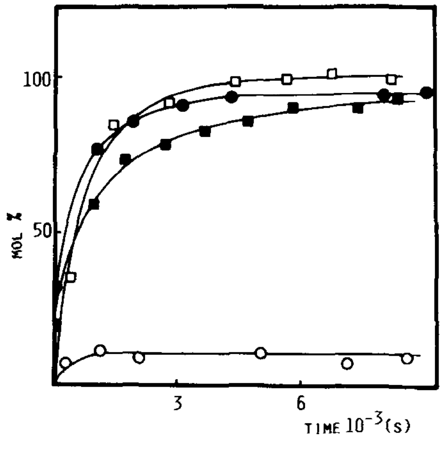

FIG. 2. Reaction profiles for the formation of 1,1-dimethoxy derivatives: propanal (□), methylpropanal (■), butanal (●), and butanone (○).

the aldehyde will be entirely converted to ketal.

To compare the hydrogenation and isomerization of the different substrates, the reactions were stopped when 50% of the stoichiometric amount of hydrogen required to completely reduce the α,β-unsaturated compound had been consumed, i.e., when 50% of the substrate had been transformed to saturated alcohol, taking into account that this would be the only process able to consume hydrogen. This was unfeasible in practice with 2-methyl-2-propen-1-ol as the maximum conversion due to the fact that the hydrogenated product was always well below 50%, since the reaction stopped indefinitely at approximately 22% conversion (hydrogenation and isomerization).

The proportions of hydrogenation and isomerization products obtained from the different α,β-unsaturated alcohols at various temperatures are given in Table 3. As can be seen, 2-methyl-3-buten-2-ol undergoes no isomerization; however, hydrogenation of the remainder of the substrates is favored with respect to the isomerization at low temperatures, although on an increase in temperature, the porportion of isomerization products increases.

In every reaction, the ratio of hydrogenation to isomerization products is constant throughout the process. Thus, the initial isomerization rate can also be determined once the initial rate of hydrogenation (obtained from the decrease in hydrogen pressure) and the aforesaid ratio are known. The initial hydrogenation and isomerization rates for each substrate at different temperatures are shown in Table 4 where we can see that the initial rate of hydrogenation increases on an increase in the number of methyl functions in the hydroxymethyl group in the sequence 2-propen-1-ol < 3-buten-2-ol < 2-methyl-3-buten-2-ol, while the methyl group bound to one of the carbons of the olefinic double bond appears to decisively influence the initial rate of hydrogenation through a steric effect, which is different at each carbon atom of the double bond. Thus, when the methyl group replaces a hydrogen in the β-carbon (2-buten-1-ol), the hydrogenation rate is scarcely different from that of the leading compound (2-propen-1-ol). On the other hand, if it replaces a hydrogen in the α-car-

TABLE 3

Percentages of Hydrogenation and Isomerization Products after Consumption of 50% of the Stoichiometric Amount of Hydrogen[a] at 0.55 MPa and Different Temperatures

Reactant	Product	Temperature (K)			
		293	303	313	323
$CH_2=CHCH_2OH$	$CH_3CH_2CH_2OH$	50.0	50.0	50.0	50.0
	CH_3CH_2CHO	14.0	15.5	16.5	28.5
$CH_3CH=CHCH_2OH$	$CH_3CH_2CH_2CH_2OH$	50.0	50.0	50.0	50.0
	$CH_3CH_2CH_2CHO$	21.0	24.5	38.5	44.5
$CH_2=C(CH_3)CH_2OH$	$CH_3CH(CH_3)CH_2OH$	16.0	13.5	10.0	7.5
	$CH_3CH(CH_3)CHO$	6.0	8.5	12.0	14.5
$CH_2=CHCH(OH)CH_3$	$CH_3CH_2CH(OH)CH_3$	50.0	50.0	50.0	50.0
	$CH_3CH_2COCH_3$	7.0	10.0	12.0	16.0
$CH_2=CHC(CH_3)_2OH$	$CH_3CH_2C(CH_3)_2OH$	50.0	50.0	50.0	50.0
	No isomerization				

[a] With the exception of 2-methyl-2-propen-1-ol, for which the corresponding values for the maximum hydrogen consumption obtained are indicated.

TABLE 4

Initial Hydrogenation and Isomerization Rates, r_0, of the Various α,β-Unsaturated Alcohols Obtained with Rh/AlPO$_4$ at 0.55 MPa and Different Temperatures

Alcohols	Temperature (K)	r_0 (mol s^{-1} g$_{\mathrm{Rh}}^{-1}$) × 10^3	
		Hydrogenation	Isomerization
$CH_2{=}CHCH_2OH$	293	5.3	1.5
	303	9.5	2.8
	313	13.0	4.3
	323	21.5	12.3
$CH_3CH{=}CHCH_2OH$	293	6.3	2.7
	303	7.5	3.7
	313	13.0	10.0
	323	17.3	15.5
$CH_2{=}C(CH_3)CH_2OH$	293	2.0	0.7
	303	2.8	1.7
	313	[a]	[a]
	323	[a]	[a]
$CH_2{=}CHCH(CH_3)OH$	293	10.8	1.5
	303	20.8	4.2
	313	41.7	10.0
	323	63.2	20.2
$CH_2{=}CHC(CH_3)_2OH$	293	31.7	0.0
	303	59.2	0.0
	313	112.8	0.0
	323	185.8	0.0

[a] The amount of hydrogen consumed was too small (Table 3) to calculate the initial rate of hydrogenation without a large degree of experimental error.

bon (2-methyl-2-propen-1-ol), the rate diminishes dramatically and the process is strongly inhibited, so much so that the process stops under our reaction conditions when only 22% of the starting product has been reacted. In addition, the amount of hydrogenated product formed from 2-methyl-2-propen-1-ol decreases with increasing temperature, and the decrease in the hydrogen pressure is so quick and small at 313 and 323 K that the initial rate of hydrogenation thus determined is subject to a high degree of experimental error and thus unreliable. So, these results were not considered, although they are obviously higher than those corresponding to lower temperatures. This behavior could be ascribed to the poisoning of the active sites by the strong (irreversible) adsorption of the formyl group of 2-methylpropanal produced in the isomerization process.

These results do not agree with those previously obtained (8) in the hydrogenation of styrene and α-methylstyrene with the same catalyst and identical experimental conditions because both reactants exhibited nearly identical catalytic activity and apparent activation energies. This showed that methyl substitution does not influence the reactivity of the olefinic double bond by an electronic or inductive effect. In the present case, the r_0 values in Table 4 are not the only ones that are different. The corresponding values of apparent activation energy, E_a, obtained from Arrhenius plots for hydrogenation as well as for isomerization and collected in Table 5, are clearly different as well.

This indicates that α,β-methyl substitution is closely related to the whole molecule and that the presence of a hydroxymethyl group, instead of a phenyl group,

TABLE 5

Apparent Activation Energies, E_a (kJ mol^{-1}), and Arrhenius Constants, ln A (mol s^{-1}, g_{Rh}^{-1}), for Hydrogenation and Isomerization of Different Substrates with $Rh/AlPO_4$

Reactant	Hydrogenation		Isomerization	
	E_a	ln A	E_a	ln A
$CH_2{=}CHCH_2OH$	35 ± 3[a]	7.0 ± 0.6	53 ± 8	15 ± 3
$CH_3CH{=}CHCH_2OH$	28 ± 4	4.0 ± 0.8	49 ± 7	14 ± 2
$CH_2{=}CHCH(CH_3)OH$	47 ± 3	12.5 ± 0.9	68 ± 3	22 ± 1
$CH_2{=}CHC(CH_3)_2OH$	47 ± 1	13.4 ± 0.3	[b]	[b]

[a] Mean ± SD.

[b] This substrate yields no isomer.

has a double effect on the catalytic activity. The first is due to an inductive or electronic action which manifests itself in the E_a values. The second is due to a steric effect, whereby adsorption of the reactant molecules is hindered to a variable degree. This contribution may be seen in the relative values of the Arrhenius constants. However, these steric and electronic effects can be better evaluated from the values of activation enthalpy, $\Delta H^\ddagger$, and activation entropy, $\Delta S^\ddagger$, obtained from the Eyring equation, which evaluates the temperature dependence of reaction rates in terms of the transition state theory. The corresponding $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for hydrogenation and isomerization are shown in Table 6.

In dealing with $\Delta H^\ddagger$ it is necessary to point out that it reflects the difference between the internal energy of the activated complex and the reactants, so it will also be related to the electronic state of the substrate (and catalyst), whereas $\Delta S^\ddagger$ (which measures the degree of order or disorder produced in formation of the activated complex) ought to be related, first, to the steric effects of reactants (and catalyst). Also, an increase in these parameters, according to the Eyring equation, indicates that electronic effects associated with the enthalpy factor diminish the reactivity, while steric effects associated with the entropy factor lead to enhancement of the reactivity. Consequently, the increase in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values in the order $CH_3{-}CH{=}CH{-}CH_2OH < CH_2{=}CH{-}CH_2OH \ll CH_2{=}CH{-}CH(CH_3)OH \simeq$

TABLE 6

Activation Enthalpies, $\Delta H^\ddagger$ (kJ mol^{-1}), and Activation Entropies, $\Delta S^\ddagger$ (J mol^{-1} K^{-1}), for Hydrogenation and Isomerization of Different Substrates with $Rh/AlPO_4$

Reactant	Hydrogenation		Isomerization	
	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
$CH_2{=}CHCH_2OH$	33 ± 3	−196 ± 10	50 ± 8	−129 ± 25
$CH_3CH{=}CHCH_2OH$	25 ± 4	−221 ± 16	48 ± 7	−134 ± 32
$CH_2{=}CHCH(CH_3)OH$	45 ± 3	−151 ± 11	66 ± 3	−75 ± 15
$CH_2{=}CHC(CH_3)_2OH$	44 ± 1	−143 ± 5	[b]	[b]

[a] Mean ± SD.

[b] This substrate yields no isomer.

$CH_2{=}CH{-}C(CH_3)_2OH$, indicates that the methyl group promotes a different behavior according to its position.

Thus, in agreement with these general ideas, the lowering of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, with respect to 2-propen-1-ol, associated with β-methyl substitution (and probably in α) indicates that the electronic effect of the methyl group, associated with the enthalpy factor, increases the reactivity (activating effect). At the same time, its steric effects promote a decrease in the degrees of freedom in the activated complex, as indicated by the decrease in $\Delta S^{\ddagger}$, leading to a diminution in the reactivity (deactivating effect). Substitution of methyl for the hydroxymethyl group has the opposite influence. In this case, the steric effects, shown in the increased $\Delta S^{\ddagger}$ values (with respect to 2-propen-1-ol), promotes an activating effect, whereas the electronic effects, through the higher values of $\Delta H^{\ddagger}$, are deactivating. Also, we have to take into account that the results obtained in isomerization are identical to those obtained in hydrogenation (Tables 4–6). This differential behavior associated with the substitution position could be ascribed to the effects of the methyl group known as "hyperconjugation" (*23*).

Furthermore, there is a relationship between the values of ln A and E_a in Table 5 (in both sets of hydrogenation and isomerization reactions) according to the most habitual expression of the "compensation effect" or "isokinetic relationship (IKR)" (*24–31*)

$$\ln A = \ln \alpha + E_a/\theta R \qquad (3)$$

where R is the gas constant, and θ is the isokinetic temperature at which identical values of reaction rate constant $k = \alpha$ are obtained. In fact, such plots of ln A versus E_a for both kinds of reactions are linear with regression coefficients over 0.99. α and θ are obtained from the slopes and intercepts and are listed in Table 7. The same values of θ are obtained within experimental error by plotting $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$, according to the general expression

$$\Delta G^{\ddagger}_{\text{const}} = -\theta R \ln K^{\ddagger} = \Delta H - \theta \Delta S^{\ddagger}. \qquad (4)$$

TABLE 7

α and θ^a, Obtained from ln A versus E_a, and θ^b, $\Delta G^{\ddagger}$, and ln $K^{\ddagger}$, Obtained from $\Delta H^{\ddagger}$ versus $\Delta S^{\ddagger}$, for Hydrogenation and Isomerization Processes

Parameter	Hydrogenation	Isomerization
α (mol s^{-1} g_{Rh}^{-1}) × 10^3	0.07 ± 0.02[a]	4 ± 3
θ^a (K)	251 ± 20	303 ± 19
θ^b (K)	249 ± 20	302 ± 20
ΔG (kJ mol^{-1})	81 ± 3	89 ± 2
ln $K^{\ddagger}$	39 ± 2	35.3 ± 0.77

[a] Mean ± SD. Uncertainties are determined by the respective standard deviations.

Thus, from slopes and intercepts we obtain respectively the values of θ and those corresponding to the equilibrium constant of the activated complex $K^{\ddagger}$ and the activation energy, $\Delta G^{\ddagger}$, also shown in Table 7. So, although the compensation effect is usually represented by Eq. (3), it may also be obtained from the entropy–enthalpy relationship. According to Boudart (*25*), the general explanation of this fact is the existence of a linear free-energy relationship (LFER), which manifests itself in a linear relation between enthalpy and entropy in the activated complex for any set of reactions of the same type, exhibiting the same value of $\Delta G^{\ddagger}$ throughout the experimental temperature range. Consequently, this constraint on $\Delta G^{\ddagger}$ is what lets us determine the set of parameters θ, α, $\Delta G^{\ddagger}$, and $K^{\ddagger}$.

Using Eq. (3), the Arrhenius expression can be written as

$$k = \alpha \exp[(E_a/R)(1/\theta - 1/T)] \qquad (5)$$

and from Eq. (4) the Eyring expression is also obtained as a function of the isokinetic parameters:

$$k/T = (k'/h) \times \exp[(\Delta H^{\ddagger}/R)(1/\theta - 1/T) + \ln K^{\ddagger}]. \qquad (6)$$

k is the reaction rate constant, k' and h are Boltzmann's and Planck's constants, and T is the absolute temperature.

Based on these results, the effect of methyl substitution on catalytic activity can be evaluated through the activation parameter E_a or $\Delta H^\ddagger$ collected in Tables 5 and 6 and the isokinetic parameters θ, α, and ln $K^\ddagger$ in Table 7. Thus, the θ value may account for the same sequence obtained for r_0 and E_a or $\Delta H^\ddagger$ if it is considered that according to Eq. (5) or (6), when the experimental reaction temperature is below θ, the reactions with lower E_a (or $\Delta H^\ddagger$) exhibit higher reaction rates, whereas above θ, the inverse is true. Indeed, we have always operated above θ where the reaction with higher E_a or $\Delta H^\ddagger$ exhibits higher reaction rates, and therefore the same sequence obtained in r_0 and E_a or $\Delta H^\ddagger$ values. Furthermore, according to the classification of Blackadder and Hinshelwood (*32*), the hydrogenation and isomerization processes, under present experimental conditions, ought to be considered entropy controlled ($\theta < T$ experimental).

On the other hand, it is interesting to note that on plotting all the values (hydrogenation and isomerization) of $\Delta H^\ddagger$ against the corresponding $\Delta S^\ddagger$ values, a very good regression coefficient (0.996, as can be seen in Fig. 3) is obtained. From the slope and intercept $\theta = 270 \pm 11$, $\Delta G^\ddagger = 76 \pm 1$, and ln $K^\ddagger = -33.7 \pm 0.6$ are obtained.

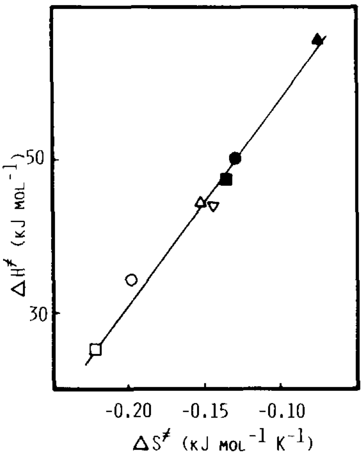

FIG. 3. Compensation effect between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for different α,β-unsaturated alcohols. $CH_2{=}CCH_2OH$: hydrogenation (○) and isomerization (●); $CH_3CH{=}CHCH_2OH$: hydrogenation (□) and isomerization (■); $CH_2{=}CHCH(CH_3)OH$: hydrogenation (△) and isomerization (▲); $CH_2{=}CHC(CH_3)_2OH$: hydrogenation (▽).

It must be taken into account (*28*) that when a compensation effect holds for a reaction series, a single common interaction mechanism can be expected. Consequently, a common transition state (TS) intermediate can be expected for both processes, i.e., isomerization and hydrogenation. Furthermore, the entropy-controlled character of the process ($\theta < T$ experimental) indicates that, on going from the ground state to the transition state, an extensive restriction in the degrees of freedom must be considered. A highly ordered common transition state, required by a concerted process, is consistent with these data. Likewise it is also noteworthy that sensitivity to solvent polarity (Fig. 1) is relatively low when compared with processes developed through a zwitterionic mechanism (*21, 33*). However, according to this sensitivity to the solvent, we have to consider a transition state with some partially developed charge because the FMO model also makes this possible (*34, 35*). Finally, we found that isomerization of the different α,β/unsaturated alcohols studied took place only when molecular hydrogen was present in the reaction and at least one hydrogen atom was present in the hydroxymethyl group (2-methyl-3-buten-2-ol does not exhibit isomerization).

On the basis of these results, we suggest a *cis*-concerted mechanism for olefin hydrogenation on a supported rhodium catalyst where the kinetic or rate-limiting step is II in Fig. 4. Here we have the three classical steps postulated by Horiuti and Polanyi (*36*). However, we think that a concerted evolution of the transition state explains the usual *cis*-addition, nonreversal character, and double-bond isomerization obtained, better than does the half-hydrogenated species classically postulated (*37, 38*). Whether or not the new bonds in the concerted mechanism form simultaneously is

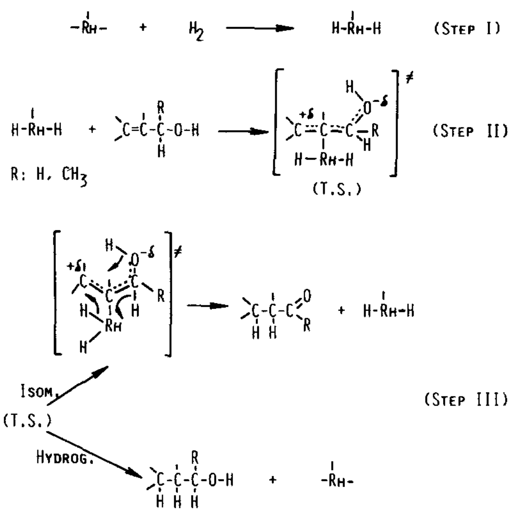

Fig. 4. Mechanism of the liquid-phase catalytic hydrogenation of the olefinic double bond on Rh/AlPO$_4$.

an open question (the limit could be the half-hydrogenated state). Therefore, the concerted character of the hydrogenation mechanism is considered according to the terminology proposed by Dewar and coworkers (*39, 40*) which distinguishes concerted reactions (taking place in a single step) from a synchronous reaction (a concerted reaction in which all the bond-breaking and bond-making processes take place in parallel).

In the present mechanism, the active sites on the rhodium surface are looked on as a surface complex (*41, 42*) with three degrees of coordinative unsaturation where it is possible to adsorb two hydrogens and an olefin at the same time. The transfer of the two hydrogens to the double bond through a concerted process leads directly to alkane formation. The isomerization reaction is developed throughout the intramolecular 1,3-sigmatropic shift of the hydrogen atom of the hydroxy group toward the α-carbon [i.e., via an intermediate with a bridged hydrogen between α-C and O, according to the terminology of Naito and Tanimoto (43)], while the hydrogen atom of the hydroxymethyl group is transferred to Rh which simultaneously gives one of its bonded hydrogens to the β-carbon. According to Ponec (*44*), interaction with the catalyst enables removal of the symmetry restrictions imposed by the Woodward–Hoffman rules in these thermally forbidden pericyclic reactions. In agreement with this, the homogeneous catalytic hydrogenation of alkenes (*45*), as well as hydrogenolysis of the C–O bond on metals (*46*), appears similarly to take place according to a concerted process.

Consequently, the participation of two different and specific active sites is not considered in the hydrogenation and isomerization reactions (with three and two coordinative insaturations, ^{3}M and ^{2}M, respectively) as postulated by Smith and co-workers (*47, 48*) for the hydrogenation and isomerization of (+)-apopinene. On the other hand, this kind of active site where the simultaneous adsorption of hydrogen and olefin is obtained can explain the uncommon kinetic order obtained. Thus, the reaction order with respect to hydrogen pressure higher than unity and with respect to olefin concentration lower than zero may be interpreted, according to Siegel and Garti (*49*), as a consequence of a different number of rhodium surface atoms that are able to act as active sites for each hydrogen pressure, while for every olefin concentration there is a carbonilic double-bond concentration (as a consequence of the isomerization process) able to compete with the olefinic double bond for adsorption. In this sense, we have previously described (*9, 50*) the retarding effect of the formyl group in olefinic double-bond hydrogenation in some α,β-unsaturated aldehydes with Rh/AlPO$_4$ catalysts.

CONCLUSIONS

On the basis of these results we may conclude that the Rh/AlPO$_4$ catalyst capable of selectively hydrogenating the olefinic double bond in the presence of a variety of functions is not so selective in the case of α,β-unsaturated alcohols (and probably in other olefins) possessing one hydrogen atom in the α-carbon with respect to the double bond and one heteroatom in the β-position with another hydrogen atom. In such cases, isomerization side reactions may develop, yielding carbonyl (or the corresponding unsaturation at the heteroatom), the extent of which increases as the temperature increases. So, here we have an interesting difference between the catalytic behavior of Ni- and Rh-supported catalysts: the former does not exhibit (*12*) such isomerization activity.

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