The Mechanism of Liquid-phase Catalytic Hydrogenation of the Olefinic Double Bond on Supported Nickel Catalysts

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The liquid-phase catalytic hydrogenation of several styrene derivatives, PhCH=CHR (R = H, CH_2OH, CHO, COMe, CO_2H, and CO_2Me), has been carried out at 293–333 K with 0.41 MPa of initial hydrogen pressure on nickel catalysts at 20 wt% supported on Al_2O_3, SiO_2, and on two different types of $AlPO_4$. The metal–support interaction effects as well as the substituent effects can be evaluated through several isokinetic parameters obtained due to the existence of a linear correlation between the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ (and between $\ln A$ and E_a) known as the 'compensation effect.'

A correlation between the reaction rates and the σ-parameters of the substituents within the context of the Yukawa–Tsuno equation is also obtained. The results for R substituents indicate the activating effect of electron-releasing groups. The results obtained considering the values of (r) and ρ, close to zero, when the substituents R′ in PhCH=CHCOR′ are considered, show the low dependence of the reaction rate on the electron-releasing or electron-withdrawing character of R′. On the basis of these results, we suggest a *cis*-concerted mechanism for the liquid-phase catalytic hydrogenation of the olefin double bond on supported nickel catalysts.

Metal-catalysed olefin hydrogenation and related reactions are generally supposed to proceed according to the Horiuti–Polanyi mechanism,[1] which is able to explain not only the observed *cis*-addition of hydrogen but also the fact that olefins are sometimes isomerized by hydrogenation catalysts, and that catalytic deuteriation of an olefin leads to products containing more and fewer than two atoms of deuterium per molecule as well as the unexpected formation of *trans*-addition products in some hydrogenations.

However, some controversy seems to exist in the literature with respect to the structure of the intermediates π-bonded,[2] α,β-diadsorbed,[3,4] or π-allyl species;[5] to the associative or dissociative character;[6] and to the concerted, homolytic, or heterolytic nature of the rate-determining step.[7,9]

With respect to this, previous work[9–12] on the liquid-phase catalytic hydrogenation of the olefinic double bond of several substrates on supported nickel catalysts indicated that the independence of the substrate concentration as well as that of the hydrogen pressure (zero-order kinetics where the catalytic reaction rate activity, r, is identical with the reaction constant, k) was described, within the framework of the Langmuir–Hinshelwood kinetic models, by a classical, non-competitive[13] Hortiuti–Polanyi-type mechanism, with interconversion between monoadsorbed and diadsorbed species and with the formation of a π-allylic species with delocalization over all three carbon atoms.

On the other hand, in a previous paper,[12] the existence of an 'isokinetic relationship,' i.k.r. or 'compensation effect' was obtained in the liquid-phase catalytic hydrogenation of allyl alcohol (prop-2-en-1-ol) and its own methyl derivatives, methallyl alcohol (2-methylprop-2-en-1-ol) and crotyl alcohol (but-2-en-1-ol); this fact was associated with the existence of a linear free-energy relationship, l.f.e.r.

With respect to this, the present paper reports the results of the liquid-phase catalytic hydrogenation of several styrene derivatives PhCH=CHR (R = H, CH_2OH, CHO, COMe, CO_2H, and CO_2Me, respectively) carried out with the same supported nickel systems previously employed as catalysts in the hydrogenation of allyl alcohols,[12] in order to confirm the existence of an i.k.r. as a general pattern of behaviour in the liquid-phase catalytic hydrogenation processes.

Based on these results, we obtained additional information regarding the nature of the influence of the substituents and the metal–support interaction effects on the mechanism of the metal-catalysed olefinic double-bond hydrogenation.

Experimental

Catalysts.—Systems containing 20 wt% nickel were prepared by impregnation of the supports to incipient wetness with 10 mol dm^{-3} aqueous nickel(II) nitrate following the procedure previously described.[10,14] They were dried, crushed, and screened to a particle size <0.149 mm (100 mesh size), reduced in an ultrapure hydrogen stream (1.7 $cm^3\ s^{-1}$) at 673 K for 3 h, and then cooled to room temperature in the same hydrogen stream and stored in sealed glass bottles until required.

Four different supports were used. Their detailed synthetic procedures, textural properties (surface area, pore volume, and main pore diameter) determined by nitrogen adsorption, and surface acid–base properties determined by a spectrophotometric method have been published elsewhere.[15–18] They included commercial silica (Merck Kieselgel 60; 70–230 mesh; surface area 380 $m^2\ g^{-1}$), commercial alumina (Merck acidic for chromatography; surface area 73 $m^2\ g^{-1}$), and two aluminium orthophosphates prepared by precipitation from $AlCl_3{\cdot}6H_2O$ and H_3PO_4 (85 wt%) with aqueous ammonia ($AlPO_4$-F; surface area 181 $m^2\ g^{-1}$) or with propylene oxide ($AlPO_4$-P, surface area 210 $m^2\ g^{-1}$).

The metal surface areas, S, of different nickel supported catalysts have been previously obtained[12] from the average crystallite diameter, obtained by X-ray diffraction according to the method of Moss[19] as described elsewhere[12,20] (Ni/Al_2O_3 = 26.8, Ni/SiO_2 = 44.5, $Ni/AlPO_4$-P = 32.2, and $Ni/AlPO_4$-F = 55.6 $m^2\ g^{-1}$, respectively).

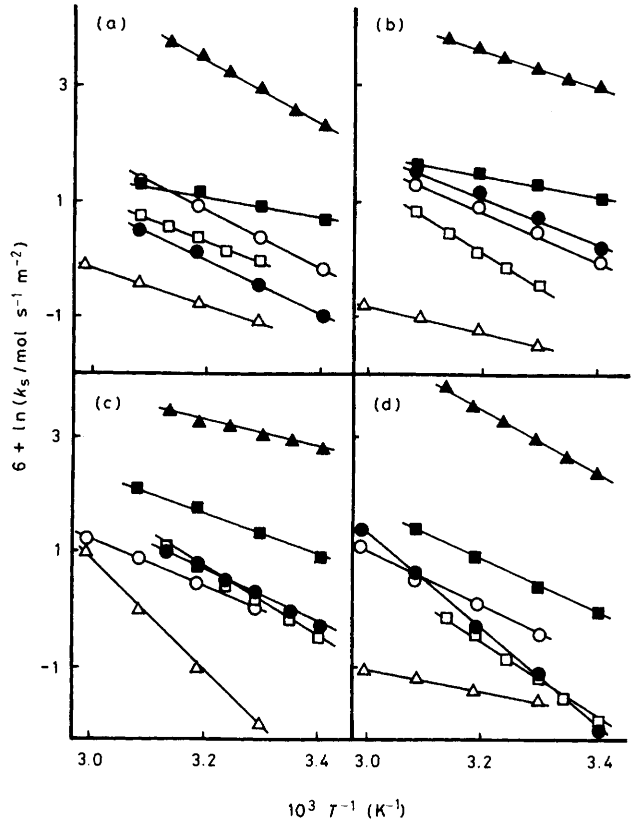


Figure 1. Arrhenius plots for the liquid-phase hydrogenation of styrene derivatives PhCH=CHR on supported nickel catalysts: (a) Ni/AlPO$_4$-P; (b) Ni/Al$_2$O$_3$; (c) Ni/SiO$_2$; and (d) Ni/AlPO$_4$-F and R = H (▲); COMe (●); CO$_2$H (□); CO$_2$Me (■); CH$_2$OH (○); and CHO (△).

Apparatus, Materials, and Procedure.—According to the procedure previously employed,[9–12,21] hydrogenations were carried out in a closed vessel, under vigorous shaking in a conventional low-pressure hydrogenator (Parr Instrument Co., Md. 3911) equipped with a manometer which constantly monitored the hydrogen pressure in the isolated reaction vessel (500 cm^3). The reaction temperature was controlled by pumping water from a thermostatic bath through the vessel jacket, with an accuracy of ±0.5 K.

Styrene, methyl cinnamate, cinnamaldehyde, and cinnamyl alcohol were obtained from Merck p.a., (*E*)-cinnamic acid was obtained from FEROSA, and benzylideneacetone from Ega-Chemie. They were all purified by distillation under reduced pressure and then passed through active acidic aluminium oxide powder for chromatography (Merck), activated at 673 K in flowing ultrapure nitrogen. Hydrogen (99.999%; S.E.O.) and the solvents methanol, ethanol, propan-1-ol, propan-2-ol, and butan-1-ol (p.a. 99%; Panreac) were used without further purification.

Most reactions were carried out in methanolic solutions (1 mol dm^{-3}; 25 cm^3) of substrate, under an initial hydrogen pressure of 0.41 MPa with catalyst (0.15–0.60 g) and temperatures in the range 293–333 K. One set of reactions employing several solvents was carried out at 313 K with the catalyst Ni/AlPO$_4$-F in the hydrogenation of styrene and (*E*)-cinnamic acid.

The initial reaction rates were calculated by taking the initial slope of the plot of the hydrogen pressure decrease at the manometer *versus* time. As these plots were always linear up to 80–90% conversion, the determination was straightforward and reproducible to within *ca.* 6%. Taking into account the zero-order kinetics obtained[9–12] with respect to the olefin concentration as well as to the hydrogen pressure, these initial reaction rates so obtained can be considered as the corresponding reaction constant values, *k*. Thus, the specific reaction rate constant or areal rate, k_s, defined as the activity per unit surface area of nickel metal in mol s^{-1} m$_{Ni}^{-2}$, was obtained from the initial reaction rate and the metallic surface area, *S*, of the catalyst.

The reaction products were analysed by g.l.c. on a Hewlett-Packard 5830 gas chromatograph fitted with an H.P. 18850 g.c. terminal, equipped with a column packed with 5% poly(phenyl ether) in 80/100 Chromosorb G AW-DMCS. The only products consistently detected were those corresponding to unsaturated or saturated substrates. Neither isomerization nor hydrogenolysis products were detected.

Results and Discussion

The selected working conditions are the same as in previous work[12] in order to avoid internal and external hydrogen-diffusion control. This effect of external diffusion was checked by reducing the shaking rate from 300 to 100 strokes min^{-1}. The reaction rates were independent of the agitation speed over 200 strokes min^{-1}. The average particle size of the catalysts used (<0.149 mm) was such that the reactions were not influenced by internal diffusion. Consequently, in the range of operating variables, the kinetic data, summarized in Figure 1, are free of transport influences.

From Figure 1 we can see the evolution of the catalytic activity with temperature; we applied the Arrhenius equation to the data to obtain the corresponding values of apparent activation energies, E_a, and Arrhenius constants, ln *A*, collected in Table 1. They are within range of those previously obtained from studies of the catalytic hydrogenation of the olefinic double bond in other substrates.[9–12]

In this connection the Eyring equation also evaluates the temperature dependence of reaction rates in terms of transition-state theory by separating the enthalpy, $\Delta H^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$, components. Their corresponding values obtained by plotting $\ln k_s T^{-1}$ against T^{-1} are also shown in Table 1.

Furthermore, there is a relationship between the values of ln *A* and E_a, in Table 1, according to the expression of the 'compensation effect' or i.k.r. [equation (1)][22,23] where R is the

$$\ln A = \ln \alpha + E_a/\theta R \qquad (1)$$

gas constant and θ is the isokinetic temperature at which identical values of areal rates $k_s = \alpha$ are obtained. Such plots of ln *A vs.* E_a for each substrate, for all catalysts, as well as the plots of ln *A vs.* E_a for each catalyst, for all substrates, were linear with regression coefficients >0.99 (Figure 2). From the slopes and intercepts, α and θ parameters were obtained for every substrate (θ_s, α_s) and for every catalyst (θ_c, α_c). They are collected in Tables 2 and 3, respectively.

These Tables also show the values of the equilibrium constant of the activated complex, $K^{\ddagger}$, and the activation free energy, $\Delta G^{\ddagger}$, obtained according to the general expression (2). Thus,

$$\Delta G^{\ddagger}_{\text{const}} = -\theta R \ln K^{\ddagger} = \Delta H^{\ddagger} - \theta \Delta S^{\ddagger} \qquad (2)$$

from slopes and intercepts of the plots of $\Delta H^{\ddagger}$ against $\Delta S^{\ddagger}$ we obtained values of θ, $\Delta G^{\ddagger}$, and $K^{\ddagger}$ for each substrate (θ_s, $\Delta G^{\ddagger}_s$, and $K^{\ddagger}_s$) and each catalyst (θ_c, $\Delta G^{\ddagger}_c$, and $K^{\ddagger}_c$).

According to Boudart,[24] the general explanation for this fact is the existence of an l.f.e.r. manifesting itself in a linear relationship 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 $\Delta G^{\ddagger}$ lets us determine a set of parameters (θ_c, α_c, $\Delta G^{\ddagger}_c$, and $K^{\ddagger}_c$) closely associated with the catalysts, and another set (θ_s, α_s, $\Delta G^{\ddagger}_s$, and $K^{\ddagger}_s$) exclusively related to the substrates.

Table 1. Apparent activation energies, E_a (kcal mol^{-1}),* Arrhenius constant, ln A, activation enthalpies, $\Delta H^{\ddagger}$ (kcal mol^{-1}), and activation entropies, $\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1}) with their respective standard deviations, for the catalysts and different substrates PhCH=CHR.

R	Activation parameter	Catalyst			
		Ni/Al_2O_3	Ni/SiO_2	$Ni/AlPO_4$-P	$Ni/AlPO_4$-F
H	E_a	6.6 ± 0.2	4.4 ± 0.1	10.8 ± 0.3	11.0 ± 0.2
	ln A	0.5 ± 0.4	−3.0 ± 0.2	7.1 ± 0.5	7.5 ± 0.3
	$\Delta H^{\ddagger}$	6.0 ± 0.3	3.8 ± 0.1	10.3 ± 0.3	10.4 ± 0.2
	$\Delta S^{\ddagger}$	−60.1 ± 0.9	−67.1 ± 0.4	−47.0 ± 1.0	−46.0 ± 0.6
COMe	E_a	9.0 ± 0.1	10.2 ± 0.1	10.0 ± 0.8	16.5 ± 0.3
	ln A	1.9 ± 0.2	3.9 ± 0.1	2.0 ± 1.0	12.5 ± 0.5
	$\Delta H^{\ddagger}$	8.4 ± 0.1	9.6 ± 0.1	9.4 ± 0.7	15.9 ± 0.3
	$\Delta S^{\ddagger}$	−57.2 ± 0.4	−53.4 ± 0.1	−56.7 ± 0.3	−36.1 ± 0.9
CO_2H	E_a	13.0 ± 0.5	13.0 ± 0.8	8.0 ± 0.1	13.7 ± 0.1
	ln A	7.4 ± 0.8	8.0 ± 1.0	−0.7 ± 0.2	7.9 ± 0.2
	$\Delta H^{\ddagger}$	12.4 ± 0.5	12.4 ± 0.8	7.6 ± 0.5	13.1 ± 0.1
	$\Delta S^{\ddagger}$	−46.0 ± 1.0	−44.0 ± 2.0	−62.1 ± 0.1	−45.2 ± 0.4
CO_2Me	E_a	3.8 ± 0.1	7.1 ± 0.1	4.1 ± 0.1	8.9 ± 0.2
	ln A	−6.3 ± 0.2	−0.2 ± 0.2	−6.1 ± 0.1	1.4 ± 0.3
	$\Delta H^{\ddagger}$	3.2 ± 0.1	6.5 ± 0.1	3.5 ± 0.1	8.3 ± 0.2
	$\Delta S^{\ddagger}$	−73.5 ± 0.4	−61.5 ± 0.3	−73.2 ± 0.3	−58.2 ± 0.7
CH_2OH	E_a	8.6 ± 0.3	7.8 ± 0.2	9.8 ± 0.3	10.2 ± 0.2
	ln A	1.0 ± 0.4	−0.3 ± 0.3	2.9 ± 0.5	2.7 ± 0.3
	$\Delta H^{\ddagger}$	8.1 ± 0.3	7.2 ± 0.2	9.2 ± 0.3	9.6 ± 0.2
	$\Delta S^{\ddagger}$	−59.0 ± 0.9	−61.8 ± 0.7	−55.0 ± 1.0	−55.6 ± 0.7
CHO	E_a	5.1 ± 0.2	19.6 ± 0.2	6.2 ± 0.1	4.5 ± 0.2
	ln A	−6.9 ± 0.3	17.3 ± 0.4	−4.7 ± 0.2	−8.1 ± 0.3
	$\Delta H^{\ddagger}$	4.5 ± 0.2	19.0 ± 0.2	5.5 ± 0.1	3.8 ± 0.2
	$\Delta S^{\ddagger}$	−74.8 ± 0.7	−26.6 ± 0.7	−70.5 ± 0.4	−77.3 ± 0.6

* 1 cal = 4.184 J.

Table 2. Values of ln α_c and θ_c^a obtained from the representation of ln A *vs.* E_a and values of θ_c^b, $\Delta G_c^{\ddagger}$, and ln $K_c^{\ddagger}$, obtained from the representation of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$. Uncertainties are determined by their respective standard deviation.

Catalyst	ln α_c	θ_c^a/K	θ_c^b/K	$\Delta G_c^{\ddagger}$/kcal mol^{-1}	ln $K_c^{\ddagger}$
$Ni/AlPO_4$-P	−15 ± 2	273 ± 40	275 ± 40	23 ± 1	−45 ± 7
Ni/Al_2O_3	−12 ± 2	323 ± 50	292 ± 50	25 ± 2	−43 ± 8
Ni/SiO_2	−10 ± 1	365 ± 20	358 ± 20	28 ± 1	−40 ± 2
$Ni/AlPO_4$-F	−14 ± 2	301 ± 40	278 ± 40	25 ± 2	−45 ± 7

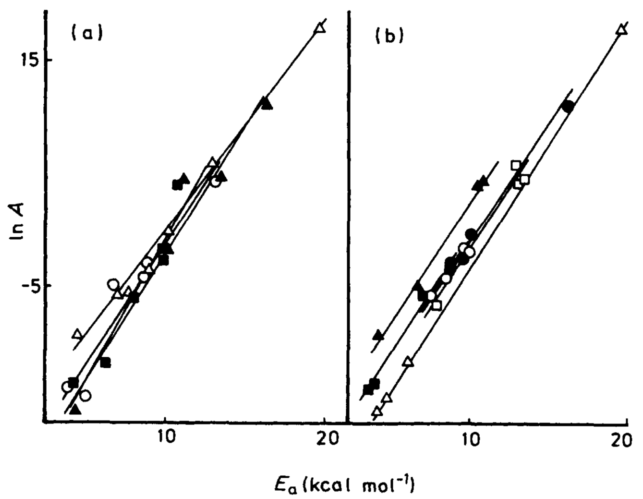


Figure 2. Compensation-effect plots (a) for each substrate, with all the catalysts: (■) $Ni/AlPO_4$-P; (○) Ni/Al_2O_3; (△) Ni/SiO_2; and (▲) $Ni/AlPO_4$-F and (b) for each catalyst with all the substrates PhCH=CHR, for R = H (▲); COMe (●); CO_2H (□); CO_2Me (■); CH_2CH (○); and CHO (△).

From equation (1), the Arrhenius expression can be written as equation (3) and from equation (2) the Eyring expression is also

$$k_s = \alpha \exp[(E_a/R)(1/\theta - 1/T)] \qquad (3)$$

obtained as a function of the isokinetic parameters [equation (4)].

$$k_s = (kT/h)\exp[(\Delta H^{\ddagger}/R)(1/\theta - 1/T) - (\Delta G^{\ddagger}/R\theta)] \quad (4)$$

Based on these results, the effects of metal–support interactions as well as the substituent effects on specific catalytic activity (shown in Figure 1) can be evaluated through the activation parameters (E_a and ln A or $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) collected in Table 1 and the isokinetic parameters (θ and α; or θ, $\Delta G^{\ddagger}$, and $K^{\ddagger}$), in Tables 2 and 3, by using equations (3) or (4). Thus, θ_c- and $\Delta G^{\ddagger}{}_c$-values may account for the sequences obtained for r_A in the hydrogenation of each substrate:

$$Ni/SiO_2 > Ni/Al_2O_3 > Ni/AlPO_2\text{-P} > Ni/AlPO_4\text{-F}$$

while the values of θ_s and $\Delta G^{\ddagger}{}_s$ can explain the sequences obtained as a consequence of the influence of the substituent effects on the reactivity:

$$R = H > CO_2Me > CH_2OH > COMe > CO_2H > CHO$$

Table 3. Values of ln α_s and θ_s^a obtained from the representation of ln A *vs.* E_a and values of θ_s^b, $\Delta G_s^\ddagger$, and ln $K_s^\ddagger$, obtained from the representation of $\Delta H^\ddagger$ *vs.* $\Delta S^\ddagger$. Uncertainties are determined by their respective standard deviation.

R	ln α_c	θ_c^a (K)	θ_c^b (K)	$\Delta G_c^\ddagger$ (kcal mol^{-1})	ln $K_c^\ddagger$
H	-10.0 ± 0.1	320 ± 2	317 ± 2	25.0 ± 0.1	-40 ± 1
COMe	-11.5 ± 1.0	348 ± 30	338 ± 30	28.0 ± 1.0	-41 ± 4
CO_2H	-13.3 ± 2.0	315 ± 40	294 ± 40	25.9 ± 2.0	-45 ± 6
CO_2Me	-12.4 ± 1.0	315 ± 30	306 ± 30	25.7 ± 2.0	-43 ± 5
CH_2OH	-10.9 ± 2.0	368 ± 50	353 ± 50	28.9 ± 3.0	-41 ± 6
CHO	-15.3 ± 0.3	304 ± 4	301 ± 4	27.0 ± 0.3	-45 ± 1

Table 4. Results of application of the Yukawa–Tsuno equation $\lg k_s/k_s\varphi = \rho_0\sigma + \rho_0(r)(\sigma^+ - \sigma)$ to R substituents in PhCH=CHR.

Catalyst	ρ_0	(r)	r^a
$Ni/AlPO_4$-P	-1.67	1.06	0.960
Ni/Al_2O_3	-2.53	0.05	0.911
Ni/SiO_2	-0.97	1.76	0.975
$Ni/AlPO_4$-F	-2.83	0.13	0.938

[a] Correlation coefficient.

Table 5. Results of application of the Yukawa–Tsuno equation $\lg k_s/k_s\varphi = \rho_0\sigma + \rho_0(r)(\sigma^+ - \sigma)$ to R′ substituents in PhCH=CHCOR′.

Catalyst	ρ_0	(r)	r^a
$Ni/AlPO_4$-P	-1.72	0.56	0.986
Ni/Al_2O_3	-1.18	0.76	0.771
Ni/SiO_2	0.72	1.50	0.919
$Ni/AlPO_4$-F	0.98	1.15	0.671

[a] Correlation coefficient.

Table 6. Solvent effect on the catalytic activity, k_s, of $Ni/AlPO_4$-F in the hydrogenation of styrene and (*E*)-cinnamic acid.

Solvent	ε^a (Debye)	10^8 k_s (mol s^{-1} m$_{Ni}^{-2}$) Styrene	(*E*)-Cinnamic acid
Methanol	32.7	685.25	12.80
Ethanol	24.5	393.32	1.07
Propan-1-ol	20.1	298.40	0.31
Propan-2-ol	18.3	251.96	0.20
Butan-1-ol	17.1	241.79	0.16

[a] Dielectric constants of the solvents.

On the other hand, the existence of an l.f.e.r. also manifests itself in the correlation between the reaction rates and the σ-parameters of the substituents within the context of the Yukawa–Tsuno equation (5).[25,26] This is a modification of the Hammett equation,[27] which takes into account the extent of the additional resonance contribution throughout the values of (*r*), by employing a two-parameter correlation; a large (*r*)

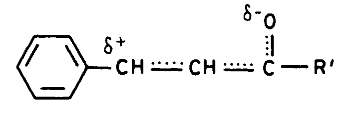
$$\log(r_A/r_A{}^\circ) = \rho\sigma + \rho(r)(\sigma^+ - \sigma) \qquad (5)$$

corresponding to a reaction with a large resonance contribution, whereas when (*r*) is zero the equation is identical with the original Hammett equation.[27] Equation (5) contains one set of resonance constants, σ^+, for electron-donating substituents; however, when there is direct conjugation with an electron-rich centre, an equation analogous to equation (5) ought to be employed, but using σ^-, one set of resonance constants for electron-withdrawing substituents, instead of σ^+. Thus, the σ^+-values reflect direct resonance interaction between a substituent, R, acting as an electron donor and a cationic reaction centre, while the σ^- set indicates a direct resonance interaction of R with an electron-rich reaction site. The correlation is not only obtained for styrene derivatives PhCH=CHR (R = H, CO_2Me, CH_2OH, COMe, CO_2H, and CHO) but also for cinnamoyl derivatives PhCH=CHCOR′ (R′ = Me, OH, OMe, and H). The substituent constant values employed were obtained from Exner.[28]

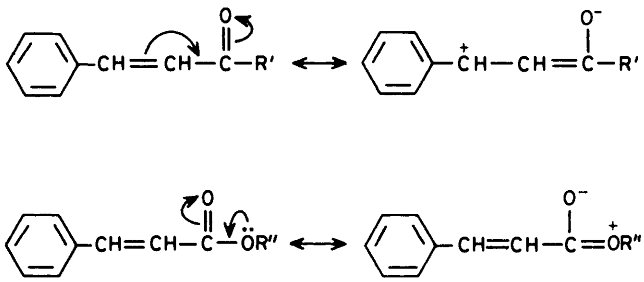
The results obtained in the correlation analysis by least-squares multiple regression between the corresponding values of areal rates of different catalysts at 313 K (Figure 1) and R substituents are given in Table 4. Those with R′ are in Table 5.

As can be seen, a very good fit is obtained with $Ni/AlPO_4$-P and Ni/SiO_2 catalysts, while with Ni/AlPO-F, and specially with Ni/Al_2O_3, the results are not so favourable. However, in general terms we may assume the validity of the treatment within the context of the Yukawa–Tsuno equation, which reflects a recognition of the variable extent of resonance participation in the reaction mechanism according to the values of $(r) > 0$. The negative values of ρ between −0.97 and −2.83 (Table 4), when the R substituent is considered, indicate the activating effect of the electron-releasing groups, while ρ-values very close to zero (Table 5), for the R′ substituent, show the low dependence of the reaction rate on the nature of R′. Accordingly, these facts account for an intermediate in the transition state as in structure (**I**), whose relative stability is determined by the extension of the resonance between the carbonyl group of R and the olefinic bond.

(**I**)

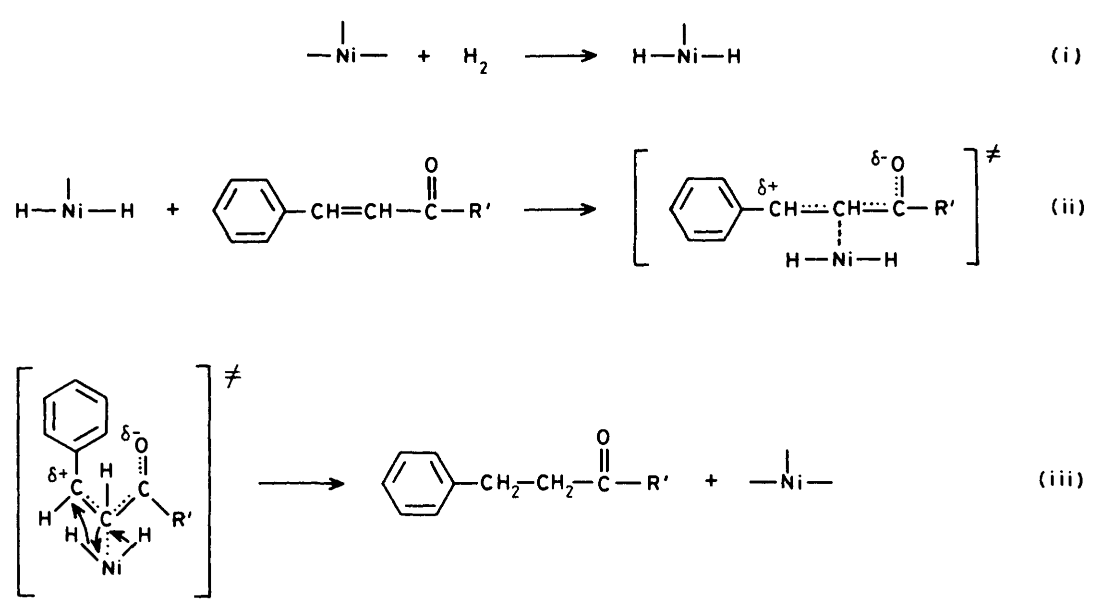


Such a structure represents the overall electron distribution resulting from the tautomerism shown in Scheme 1.



Scheme 1.

The contribution of this polarization can also be estimated from the relative influence of different solvents because the dielectric constant of a solvent plays an important role in its ability to accommodate a separation of charge. Thereby, when this influence is determined for styrene, R = H, and for (*E*)-



Scheme 2.

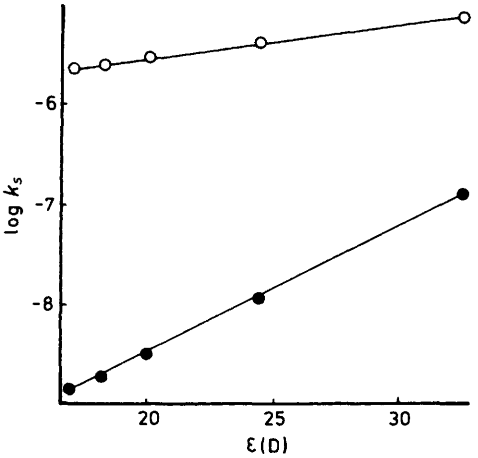


Figure 3. Influence of dielectric constant, ε, of different solvents on the catalytic activity of Ni/AlPO$_4$-F catalyst in hydrogenation of styrene (○) and (*E*)-cinnamic acid (●) at 313 K.

cinnamic acid, R = CO_2H (Table 6), we can observe in Figure 3 how the sensitivity towards the solvent effect increases almost five times due to the effect of the acid group, with respect to styrene.

Likewise it is also noteworthy that the sensitivity to solvent polarity in both cases is relatively small when compared with processes developed through a zwitterionic mechanism.[29] Conversely, its behaviour may be better exemplified by a Diels–Alder process.[30] In this sense, the low values of ρ obtained (Tables 4 and 5) also account for a concerted mechanism because transition states with partially developed charges show very high ρ-values; for instance nitration of benzene derivatives exhibits a ρ-value of -6.53.[30] The Frontier Molecular Orbital (FMO) model also makes it possible to interpret the existence of small ρ-values in concerted reactions.[31,32]

This concerted character can also be accounted for by consideration of the kinetic parameters presented in Table 1. Thus, the $\Delta S^{\ddagger}$ (and ln *A*) values are largely independent of reaction rates (Figure 1) while the changes in the energy term $\Delta H^{\ddagger}$ (or E_a) are reflected in these values because the $\Delta H^{\ddagger}$-values are considerably larger (3–16 kcal mol^{-1}) than those of $\Delta S^{\ddagger}$ (0.026–0.077 kcal mol^{-1} K^{-1}). In addition, the low values of $\Delta S^{\ddagger}$ indicate that, on going from the ground state to the transition state, an extensive restriction in degrees of freedom must be considered. A highly ordered transition state, required by a concerted process, is consistent with all these data.

On the basis of these results, we suggest a *cis*-concerted mechanism for olefin hydrogenation on supported nickel catalysts where the kinetic or rate-limiting step is (ii) in Scheme 2. Here we have the three classical steps postulated by Horiuti and Polanyi. However, in this case we exclude the intermediate half-hydrogenated state which is also considered, in reactions at relatively low hydrogen pressures, as the limiting step.[8,33,34] Furthermore, in order to explain the absence of double-bond isomerization throughout this intermediate, its non-reversible character also has to be postulated. A concerted evolution of the transition state explains this absence of double-bond isomerization, as well as the strict *cis*-addition habitually obtained, better than does the half-hydrogenated species classically postulated.

Whether or not the new bonds in the concerted mechanism are simultaneously formed is an open question. The concerted character of the hydrogenation mechanism is thus considered according to the terminology proposed by Dewar[35,36] which considers the differences between concerted reactions (each of which takes place in a single step) and a synchronous one (a concerted reaction where all the bond-breaking and bond-making processes take place in parallel).

Conclusions.—In the present mechanism, the active sites on the nickel surface are regarded as surface complexes[13,29,37,38] with three degrees of co-ordinative 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 throughout a concerted process, where the interaction with the catalyst removes the symmetry restrictions imposed by the Woodward–Hoffmann rules, leads directly to alkane formation.[39] In agreement with this, the homogeneous catalytic hydrogenation of alkenes,[40] as well as the hydrogenolysis of the C–O bond on metals,[41] appears to take place according to a concerted process.

On the other hand, this kind of active site, where the simultaneous and non-competitive adsorption of hydrogen and olefin occurs, can explain the zero-order kinetics with respect to hydrogen pressure and olefin concentration because, in the range of operating variables, the active sites are all (simultaneously) covered with both reactant molecules. Consequently, the reaction rate is only determined by the number of active sites present during the reaction. This number is determined not only by the metal surface area (related to the catalyst weight and metal dispersion) but also by the density of active sites on the metal surface, which is closely associated with the metal–support interaction effects.[20]

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