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$AlPO_4$-Supported Rhodium Catalysts

IV. Individual and Competitive Hydrogenation of Styrene and α-Methylstyrene

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Hydrogenation rates of the olefinic double bond of styrene (S) and α-methylstyrene (MS) have been measured using methanol as the solvent in the temperature range 293–323 K over $Rh/AlPO_4$ catalysts of different rhodium loading. Both organic reactants exhibited nearly identical areal rates and apparent activation energies independent of the rhodium loading (0.25 to 1 wt%) of the catalyst. The hydrogenation reaction involves a Horiuti–Polanyi mechanism modified by an irreversible adsorption of alkene. Styrene hydrogenation was also studied using other alcohols as solvents. The initial rate of hydrogenation was dependent on the polarity of the solvent. The competitive hydrogenation of both S and MS provides unambiguous evidence that the relative reactivity, $R_{MS,S}$, and the relative adsorption equilibrium constant, $K_{MS,S}$, are independent of the reaction temperature, initial hydrogen pressure, and rhodium loading. Thus, the adsorption heat and the activation energy are nearly identical for two organic reactants. © 1985 Academic Press, Inc.

INTRODUCTION

The use of $AlPO_4$, $AlPO_4$–Al_2O_3, and $AlPO_4$–SiO_2 as supports for dispersed metals has recently been described (*1–12*). Thus, metals such as Ni (*1–7*), Pd (*8*), Pt (*9*), and Rh (*10–12*) are active in hydrogenation processes. These catalysts are bifunctional and they may operate simultaneously as acid-base (*13–16*) and metallic catalysts.

The existence of metal–support interactions on $AlPO_4$-supported nickel catalysts has been invoked, based on their behavior in the liquid-phase hydrogenation of the olefinic double bond in various compounds such as 1-hexene (*1, 5*), acrolein, methyl vinyl ketone (*2*), styrene and α-methylstyrene (*3*), as well as from poisoning experiments in the liquid-phase catalytic hydrogenation of 1-hexene, using *n*-butanethiol as poison (*4*). The interaction between the support and the nickel crystallites is attributed to electron transfer between the nickel atoms and the acidic (oxidizing) sites on the surface of the support, and its extent is related to the nature of the support and metal–support ratio. However, such metal–support interaction effects have not been obtained with supported rhodium catalysts (*10–12*).

In the present paper, we report results on the liquid-phase catalytic hydrogenation of styrene (S) and α-methylstyrene (MS) on $Rh/AlPO_4$ as well as the competitive hydrogenation of both reactants. This study has been undertaken in order to compare the results with those obtained previously (*3, 4*) with supported nickel catalysts in the same reactions. The aim was to determine the differential behavior of the methyl substitution effects between Rh and Ni supported on aluminum phosphate.

EXPERIMENTAL

Support. The support was an aluminum orthophosphate obtained from $AlCl_3 \cdot 6H_2O$ (Merck p.a.) and phosphoric acid aqueous solution by gelification with propylene oxide (*15*). The support, 200–250 mesh size, was dried at 390 K for 24 h, then calcined at 920 K for 3 h, and stored in a desiccator. Its textural properties, deter-

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mined by nitrogen adsorption at liquid-nitrogen temperature, were surface area (BET method) 228 m^2g^{-1}; pore volume 0.94 ml g^{-1}, and mean pore diameter 2–4 nm.

Supported rhodium systems. The supported rhodium catalysts were prepared by impregnation of the support with an aqueous solution of $RhCl_3 \cdot 3H_3O$ (Merck p.a.) to yield a nominal 0.25, 0.5, and 1.0 wt% metal, using the incipient wetness technique. The slurry was stirred for 24 h, then the water was evaporated on a rotary vacuum evaporator and the catalyst was dried at 390 K for 24 h. The impregnated support was reduced in flowing hydrogen (200 ml min^{-1}, 99.999%, $H_2O < 3$ ppm) at 470 K for 7 min and then cooled to room temperature maintaining the same hydrogen stream.

The metal loading of the catalyst was determined by atomic absorption and is indicated as wt%.

Dispersion measurements. The metal dispersion of the rhodium-supported catalysts was measured using Transmission Electron Microscopy (TEM). TEM measurements were conducted using a Philips EM-300 electron microscope, with a better than 0.3-nm resolution and the samples were prepared by the extractive replica technique (*17*). An average of 1000–1200 particles from at least eight pictures were counted for each sample using enlarged photographs at a magnification of ×670,000 (*18*).

The average crystallite diameters, d_v (nm), were obtained from the crystallite size distributions, as determined by TEM. The surface areas of the metal, S ($m^2\ g_{Rh}^{-1}$), were obtained using the relation

$$S = \frac{6 \times 10^3}{\rho d_v} \qquad (1)$$

where ρ is the rhodium density (g ml^{-1}).

The average crystallite diameters, d_v, as well as the surface areas, were determined for catalysts with different metal loading (0.25–1 wt%).

Materials. Styrene and α-methylstyrene were commercially available (Merck) and have been distilled before use. All of the solvents were dried and distilled prior to use in order to remove catalytic poisons which might be present.

Catalytic activity. The hydrogenation of styrene (S) and α-methylstyrene (MS) was carried out in a Gerhardt low-pressure hydrogenator, equipped with a variable shaking device and with a manometer that allowed determination of the actual hydrogenation pressure in the reaction vessel. The reaction temperature was controlled by pumping water from a thermostatic bath through the vessel jacket, with an accuracy of ±0.5 K.

The reactions were carried out with 25 ml of 1 *M* methanolic solution of reactant S or MS, although some reactions were carried out in other solvents, at low pressure, and at a temperature range between 293 and 323 K. Competitive hydrogenations were carried out with a mixture of the two alkenes (0.5 *M* each) in methanol as solvent under the same conditions.

The initial reaction rates, r_0, were calculated from a least-squares fit to the slopes of linear hydrogen pressure decrease vs reaction time plots. Since this plot stayed linear to 80–90% conversion, the determination of the slopes was straightforward. The results are based on at least three repetitive measurements. The relative error was approximately 6%.

A "*t*-test" of significance, performed on the coefficients of regression, shows that these are significant at a level better than 1%. This is a measure of accuracy of fit of the data, in all experimental conditions.

The reaction products were analyzed by gas–liquid chromatography (GLC) using a Hewlett–Packard 5830 A GC with a column packed with 5% Carbowax 20M on Chromosorb G AW-DMCS 80/100. Under our experimental conditions, the only products detected were ethylbenzene and isopropylbenzene. Hydrogenation of the aromatic ring was not detected.

RESULTS AND DISCUSSION

Dispersion Measurements

The results obtained in the dispersion measurements are shown in the second and third columns of Table 1. As can be seen, the average crystallite diameters, and hence the surface areas per gram of Rh, change only slightly with increasing metal loading. On the other hand, the rhodium surface area per gram of catalyst is a linear function of the metal loading. This is due to a change in the number of particles without a measurable variation in particle size.

Individual Hydrogenation

The initial reaction rates were independent of the shaking speed above 200 strokes min^{-1}, so that above this shaking speed, the reaction rate is not controlled by gas–liquid diffusion.

Furthermore, we have found that the initial reaction rate is linear with catalyst weight below 7×10^{-3} mol min^{-1}, indicating that below this value the rate is kinetically controlled, and that the kinetic data are free from transport influences in the range of operating variables. For higher reaction rates a deviation from linearity occurs indicating that the supply of hydrogen was not rapid enough to sustain the increased consumption following the increase of rhodium in the catalyst.

On the other hand, we have also calculated the apparent reaction orders with respect to the hydrogen pressure and alkene concentration. The reaction order with respect to hydrogen, determined from the dependence of the hydrogenation rate on the initial hydrogen pressure, was first order within the pressure range 0.45–0.7 MPa and was independent of temperature (293–323 K), as shown in Fig. 1.

The reaction orders with respect to S and MS, in methanol as solvent, were determined from the dependence of the initial reaction rate on the initial concentrations. In both cases the rate was unaffected by the olefin concentration (1–3 *M*) and thus the reaction was zero order in S or MS concentration.

The considerably higher adsorptivities of unsaturated compounds as compared to the alcohol solvents used allows us to assume

TABLE 1

Average Crystallite Diameters, Metal Surface Areas, and Areal Rates in Styrene and α-Methylstyrene Hydrogenation for AlPO$_4$-Supported Rhodium Catalysts

Catalyst	d_v[a] (nm)	S[b] (m^2 g$_{Rh}^{-1}$)	T (K)	$r_{aS}10^3$[c] (mol min^{-1} m$_{Rh}^{-2}$)	$r_{aMS}10^3$[d] (mol min^{-1} m$_{Rh}^{-2}$)
0.25 Rh/AlPO$_4$	5.0	96	293	8.2	8.6
			303	11.5	12.0
			313	18.8	16.1
			323	22.6	23.6
0.5 Rh/AlPO$_4$	5.1	94	293	7.7	8.2
			303	11.9	12.0
			313	16.9	16.7
			323	22.6	23.4
1 Rh/AlPO$_4$	5.4	90	293	8.3	7.7
			303	12.7	12.0
			313	19.8	17.6
			323	29.6	22.5

[a] Average crystallite diameter from TEM micrographs.
[b] Metal surface areas.
[c] Areal rate for hydrogenation of styrene C=C bond.
[d] Areal rate for hydrogenation of α-methylstyrene side bond.

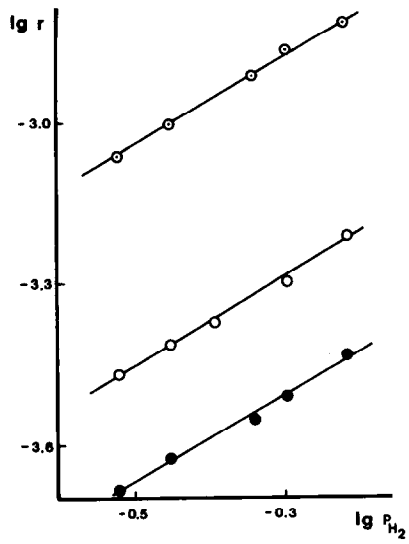

FIG. 1. Reaction orders with respect to hydrogen (1 *M* alkene in methanol, solution volume 25 ml, catalyst 0.25 $Rh/AlPO_4$); (○) styrene, 293 K; (◎) styrene, 323 K; and (●) α-methylstyrene, 293 K.

that the reaction orders with respect to MS and S are zero also in the other solvents.

The zero order with respect to S (or MS) and positive order with respect to hydrogen indicate that while the former was strongly adsorbed on the surface and its coverage was total, the latter was weakly adsorbed and its surface coverage was low. Thus, to a good approximation, the rate of hydrogenation on rhodium as simply proportional to the rate at which hydrogen strikes the sites available to it. Accordingly, the kinetic equation for the system under study can be written as

$$r = \frac{dC}{dt} = kp_{H_2}, \qquad (2)$$

where k is the reaction rate constant and p_{H_2} is the hydrogen pressure.

On the other hand, when the hydrogenation of S (or MS) was carried out to completion, it was observed that after about 80–90% conversion, the plot of percentage S (or MS) converted vs time was not linear. Explanations based on poisoning and catalyst deactivation may be ruled out because a second (or third) introduction of olefinic reactant, after the first sample had been completely converted, gave the same reaction rate as that observed for the first S (or MS) sample. This behavior is similar to observations made during the liquid-phase hydrogenation of 1-hexene, styrene, α-methylstyrene, acrolein, and methyl vinyl ketone on $Ni/AlPO_4$ catalysts (*1–5*), cyclohexene on $Rh/AlPO_4$–SiO_2 catalysts (*11*), and for the liquid-phase hydrogenation of cyclohexene on Pt/Al_2O_3 and Pt/SiO_2 by Madon *et al.* (*19*), where the order of reaction with respect to olefin changes from zero to unity because at very low concentrations the catalyst surface is "starved" of olefin molecules. Thus, our work is concerned only with the linear portion of the plot of the hydrogen pressure decrease vs reaction time, where the reaction rate is zero order with respect to S and MS.

These results together with the plot of the olefin concentration/reaction rate vs olefin concentration (Fig. 2) indicate that catalytic hydrogenation is a noncompetitive process with an irreversible chemisorption of alkene (intercept at origin) in which the cata-

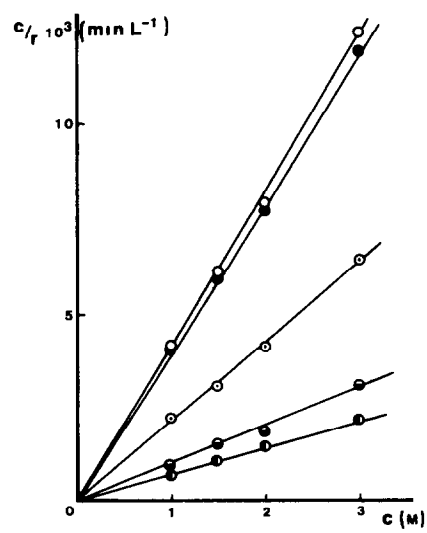

FIG. 2. Plot of [alkene molarity/rate] vs alkene molarity in methanol. Catalyst 0.25 $Rh/AlPO_4$ (rate in mol min^{-1}) (○) styrene, 0.46 MPa, 293 K; (◎) styrene, 0.61 MPa, 293 K; (◒) styrene, 0.46 MPa, 323 K; (◐) styrene, 0.61 MPa, 323 K; and (●) α-methylstyrene, 0.46 MPa, 293 K.

TABLE 2

Solvent Effect in the Initial Rate of the Styrene Hydrogenation on 0.25 Rh/AlPO$_4$ (T: 298 K; p_{H_2}: 0.46 MPa)

Solvent	r_0[a] (mol min^{-1} g$_{Rh}^{-1}$)	ε[b] (298 K)
Methanol	0.70	32.6
Ethanol	0.44	24.3
1-Propanol	0.36	20.1
2-Propanol	0.25	18.3
2-Butanol	0.24	17.5

[a] Initial hydrogenation rate.
[b] Dielectric constant.

lyst is saturated by olefin chemisorbed during reaction and hydrogen is adsorbed over those sites in which the olefin chemisorption is excluded by geometrical effects. These results are in accord with a process which occurs through the Horiuti–Polanyi mechanism (*20*).

As shown in Table 2, the hydrogenation rate is greatly affected by the change of the solvent. The best solvent is methanol since it gives rise to the highest values of reaction rate. The linear correlation between the logarithm of hydrogenation rates and the Taft substituent constant values, σ^* (or dielectric constant, ε) of the alcohols used, seem to demonstrate that the protic character of the alcohols plays an important role in the catalytic hydrogenation. The solvent probably influences the bond energies of the activated complex, by its dielectric properties, during the surface reaction. Since the slope of this correlation for cyclohexene is higher than for styrene we have to conclude that the polarization of styrene is larger than that of cyclohexene (*10*), so that styrene presents a more polar transition state (or intermediate) in line with what the classic theory of resonance predicts. In this sense, Cerveny *et al.* (*21, 22*) concluded that the solvent effect on the rate and selectivity of catalytic hydrogenation might be predicted based on the knowledge of the physical properties, particularly the dielectric constant of the solvent. However, a complex approach to reaction systems is necessary, because the investigation of any particular effect, regardless of the other effects, leads to an exaggerated simplification, and the individual results cannot be applied to other systems. Thus, multiparameter equations were suggested to reflect the effect of solvent on the course of the catalytic reaction (*23*) so that the generalization of results is feasible only by assuming a complex view of reaction systems, because all of the operative effects in the process are related to one another.

The results obtained for the areal rates, r_a, of S and MS, as a function of the metal loading, are shown in Table 1. As can be seen, the areal rates do not change with the metal loading. This fact indicates that the hydrogenation reaction is structure insensitive and thus there is no metal–support interaction on the AlPO$_4$-supported rhodium catalysts, or that the extent of this interaction is independent of the rhodium catalyst loading, differing from Ni/AlPO$_4$ (*1–5*).

Equally, the areal rates of S and MS are very similar at the same temperature and hydrogen pressure. This may be ascribed to the absence of steric hindrance in their adsorption.

The values of the apparent activation energy, E_a, obtained from Arrhenius plots in the temperature range 293–323 K, are listed in Table 3. These E_a values are low and practically do not change with the metal loading. This is due to the fact that the adsorption coefficient is low and, thus, the heat of adsorption is very similar to the true

TABLE 3

Apparent Activation Energies for Styrene and α-Methylstyrene Hydrogenation

Catalyst	E_a (kJ mol^{-1})	
	Styrene	α-Methylstyrene
0.25 Rh/AlPO$_4$	26.8	25.9
0.5 Rh/AlPO$_4$	28.1	27.0
1 Rh/AlPO$_4$	31.1	28.5

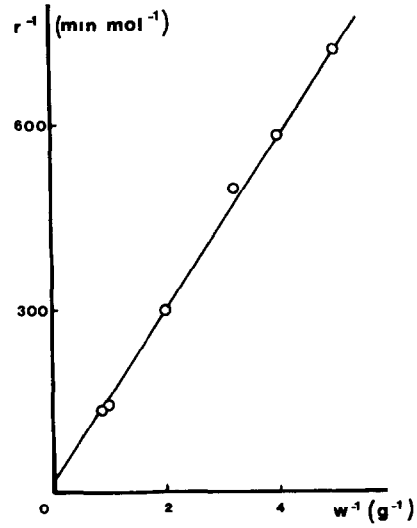

FIG. 3. Reciprocal initial rate against reciprocal mass of catalyst.

activation energy. A control by diffusion is rejected since the plot of reciprocal initial rate against reciprocal mass of catalyst ($1/r_0$ vs $1/w$) is linear with a transfer rate higher than any initial rate (Fig. 3). In Table 3, we can also see that the values of E_a of the S and MS are very similar. This shows that the methyl substitution does not influence the reactivity of the olefinic double bond by an electronic or inductive effect, in contrast to the results obtained with $Ni/AlPO_4$ catalysts (*3, 4*).

Competitive Hydrogenation

The distribution of reactants and products as a function of extent of simultaneous hydrogenation of S and MS is shown in Fig. 4.

The treatment of competitive reaction on solid catalysts (*24*) tells us that the simultaneous reaction of two reducible molecules, 1 and 2, is a competitive process when the plot of the log (C_2^0/C_2) vs log (C_1^0/C_1) is linear, where C^0 is the initial concentration and C is the concentration at time t. In our case, such a plot (Fig. 5) is linear and, thus, we can say that the simultaneous hydrogenation of S and MS is a competitive process.

The value of the slope gives the relative

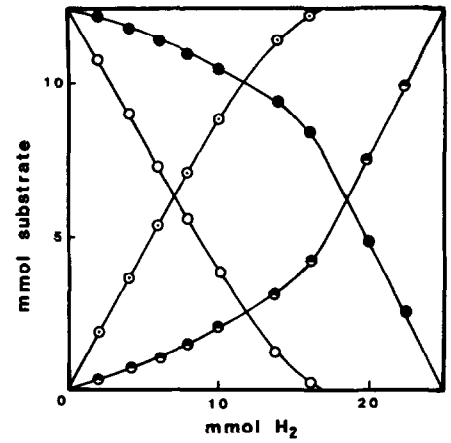

FIG. 4. Distribution of reactants and products as a function of extent of simultaneous hydrogenation of styrene and α-methylstyrene (0.5 *M* of each alkene in methanol, 0.46 MPa hydrogen pressure, solution volume 25 ml, temperature 298 K, catalyst 0.25 $Rh/AlPO_4$). (○) Styrene, (●) α-methylstyrene, (⊙) ethylbenzene, and (◓) isopropylbenzene.

reactivity of MS to S, $R_{MS,S}$. We also calculated the relative adsorption equilibrium constant, $K_{MS,S}$, using the following expression

$$R_{MS,S} = \frac{r_{MS}}{r_S} K_{MS,S}, \qquad (3)$$

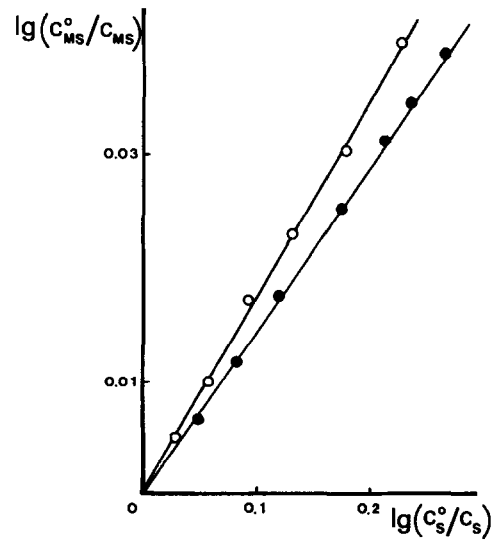

FIG. 5. Logarithmic plot of disappearance of α-methylstyrene vs styrene (0.46 MPa hydrogen pressure, catalyst 0.25 $Rh/AlPO_4$). (○) 293 K and (●) 323 K.

where r_{MS} and r_S are, respectively, the MS and S individual reaction rates. This is only valid provided that the concentrations of MS and S are high enough for r_{MS} and r_S to be independent of the concentration, as has been confirmed previously.

In this way we have obtained the $R_{MS,S}$ and $K_{MS,S}$ values at different temperatures, initial hydrogen pressures and rhodium loadings. The results are listed in Table 4. As can be seen, $R_{MS,S}$, as well as $K_{MS,S}$, are lower than unity, probably as a consequence of the steric hindrance on adsorption of the double bond of MS in relation to S. Thus, the methyl substitution delays the hydrogenation of the C=C bond. Nevertheless, the $R_{MS,S}$ and $K_{MS,S}$ values are independent of the reaction temperature, initial hydrogen pressure, and rhodium loading.

If the relative reactivity, $R_{MS,S}$, is temperature independent, the heat of adsorption as well as the activation energy must be nearly identical for the two adsorbed reactants S and MS; that is to say, the adsorption and hydrogenation of the molecules are different only in the entropy factor, thus, giving rise to the observed identity for individual hydrogenation of S and MS. This effect is equally independent of rhodium loading and initial hydrogen pressure.

On the other hand, the equilibrium adsorption constant, K (i.e., the ratio of adsorption to desorption rates) can be expressed by

$$K = \exp(\Delta S/R)\exp(-\Delta H/RT), \quad (4)$$

where ΔS is the differential entropy of adsorption and ΔH is the heat of adsorption.

Applying Eq. (4) to both S and MS we obtain

$$K_S = \exp(\Delta S_S/R)\exp(-\Delta H_S/RT) \quad (5)$$

and

$$K_{MS} = \exp(\Delta S_{MS}/R)\exp(-\Delta H_{MS}/RT). \quad (6)$$

Taking into account that

$$K_{MS,S} = K_{MS}/K_S \quad (7)$$

and that $K_{MS,S}$ is temperature independent (Table 4) we have

$$K_{MS,S} = \exp(\Delta S_{MS}/R)/\exp(\Delta S_S/R) < 1. \quad (8)$$

Thus

$$\Delta S_{MS} < \Delta S_S \quad (9)$$

and we have to conclude that the low values of $K_{MS,S}$ are determined by the entropy factor.

Upon adsorption, the olefin loses its translational freedom and rotational freedom at the double bond. The more substituted the alkene, the greater will be the entropy loss and, therefore, the methyl substitution reduces the relative reactivity, and the relative equilibrium adsorption constant. Thus, the methyl substitution only operates in the competitive hydrogenation of S and MS on Rh/AlPO$_4$ catalysts, in contrast to what occurs on Ni/AlPO$_4$ catalysts, where the methyl substitution exerts an effect in two ways. The first is by an inductive effect increasing the reactivity of the double bond, and this manifests itself in a lowering of the apparent activation energy values by about two orders of magnitude. The second is by a steric effect whereby the adsorption of the reactant molecules is hin-

TABLE 4

Relative Reactivities, $R_{MS,S}$, and Relative Adsorption Equilibrium Constants, $K_{MS,S}$, for the Competitive Hydrogenation of Styrene and α-Methylstyrene on Rh/AlPO$_4$ Catalysts

Catalyst	P_{H_2}[a] (MPa)	T (K)	$R_{MS,S}$	$K_{MS,S}$
0.25 Rh/AlPO$_4$	0.46	293	0.117	0.112
		303	0.122	0.117
		313	0.115	0.120
		323	0.123	0.118
	0.61	293	0.120	0.122
		323	0.116	0.123
0.5 Rh/AlPO$_4$	0.46	293	0.117	0.110
1 Rh/AlPO$_4$	0.46	293	0.118	0.127

[a] Initial hydrogen pressure.

dered resulting in similar areal rates for individual hydrogenation of S and MS, although the apparent activation energy for MS is smaller.

Tanaka *et al.* studied the methyl substituent effect in cyclohexanone (C) (*25, 26*) and methylencyclohexane (MeneC) (*27*) over Group VIII metal catalysts. Hydrogenation runs were conducted in cyclohexane as solvent at 303 K and atmospheric hydrogen pressure. Catalysts employed were unsupported metal powders (*25, 27*) or Al_2O_3-supported metals (*26*). In all cases they found that the methyl derivative was less reactive than the unsubstituted reactant on all the metal catalysts used. Furthermore, the relative reactivity, R, was dependent upon the reaction mechanism and the atomic radius of the metal catalyst. INDO and MINDO/2 calculations show that in the ketone we could unambiguously rule out any polar factor whereas the olefinic double bond of MeneC is significantly different from that of the methyl derivative in charge density. However, Tanaka *et al.* concluded that the methyl substituent effect upon the hydrogenation rate is due primarily to the steric hindrance in adsorption.

According to the results in Table 4, the methyl substituent effect in hydrogenation of the olefinic double bond of styrene is similar to that obtained by Tanaka *et al.* with unsupported Rh catalysts in cyclohexanone, $R = 0.033$ (*25*) and MeneC, $R = 0.21$ (*27*) or with Rh/Al_2O_3 at 0.5% (*26*) in cyclohexanone, $R = 0.134$.

Thus, in the present case, the method of the competitive reaction becomes suitable for the determination of the relative reactivity, as well as the relative adsorption equilibrium constant, since both individual reactions proceed at comparable rates.

From the results obtained we conclude that $Rh/AlPO_4$ are efficient catalysts for styrene and α-methylstyrene hydrogenation at low temperature and hydrogen pressure with a total selectivity toward hydrogenation of the olefinic double bond. The reaction can be called, according to Boudart (*28*), *structure insensitive* or *facile*. Moreover, the adsorption and hydrogenation of the two molecules are different only in the entropy factor, thus giving rise to the observed identity for individual hydrogenation of S and MS, and $R_{MS,S}$ (or $K_{MS,S}$) values lower than unity for its competitive hydrogenation.

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