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Inhibition of the Adsorption of Cyclohexene by Phenylacetylene over a Pd/Sepiolite Catalyst

Catalytic reductions by hydrogen transfer with different donors (*1, 2*) have been widely used in organic syntheses in the last few years; so much so that, in many instances, they have become useful alternatives to conventional catalytic hydrogenations with hydrogen gas. We recently showed the usefulness of catalysts obtained by supporting palladium on $AlPO_4$, $AlPO_4$–SiO_2, and $AlPO_4$–Al_2O_3 in the hydrogen-transfer reduction of various organic substrates using different hydrogen donors (*3–6*). We also showed the applicability of a catalyst supported on a Spanish sepiolite in the reduction of variously substituted double bonds ($R_1R_2C{=}CR_3G$) (*7*). We have found that phenylacetylene cannot be reduced by hydrogen transfer using cyclohexene as donor, while, under identical conditions, both styrene and α-methylstyrene are readily reduced. As the substrate to be reduced and hydrogen are adsorbed at different active sites in reductions with molecular hydrogen, we have applied the theory of competitive hydrogenations (*8–10*) to these reductions for the phenylacetylene/cyclohexene pair in order to find out the reason why phenylacetylene cannot be reduced by transfer using cyclohexene as hydrogen donor.

Supported Pd system. We used a Pd catalyst, 3% by weight, prepared by impregnation of a precursor salt (Na_2PdCl_4) over a sepiolite of the Pansil (PS) variety, supplied by Tolsa S.A. and extracted from their ores in Vallecas (Spain). Its surface area, determined by the BET method, pore volume, and average pore diameter were 280 $m^2\,g^{-1}$, 0.43 ml g^{-1}, and 3.5 nm, respectively. It was calcined at 673 K and doped with NaOH up to a Na^+/Pd ratio of 4. The catalyst synthesis was described elsewhere (*7*). The average metal particle size, determined by transmission electron microscopy (TEM) was 4 nm.

Hydrogen-transfer reductions were carried out on a Berghof Heiz reactor by using 5×10^{-3} mol of the substrate, 0.05 g of catalyst, and enough donor (cyclohexene) to make up a volume of 6 ml. The reaction temperature was varied between 383 and 413 K.

Reduction processes with hydrogen gas were described elsewhere (*9*), and the reaction conditions used are given in Table 1.

The results obtained in the competitive hydrogenations between phenylacetylene and cyclohexene can be interpreted by applying the Langmuir kinetics on the basis of the equation proposed by Rader and Smith (*10*). This allows one to calculate relative adsorption coefficients, $D_{A,B}$, from data obtained from the competitive reaction and from the rate constants of the individual reactions in the zero-order region with respect to the substrate concentration:

$$\log (C_A^0/C_A) = R_{A,B} \times \log (C_B^0/C_B) \quad (1)$$

$$D_{A,B} = (k_B/k_A) \times R_{A,B}. \quad (2)$$

The relative reactivity of phenylacetylene with respect to styrene, $R_{A,B}$, was calculated by two procedures, namely: (a) by applying the modified theory of competitive hydrogenations, Eq. (3), to the consecutive reaction phenylacetylene-styrene-ethylbenzene

$$\log(C_A^0/C_A) = R_{A,B} \times \log\{C_B^0/[C_B - (C_A^0 - C_A)]\}, \quad (3)$$

where C_A^0 and C_B^0 are the phenylacetylene and styrene concentrations, respectively,

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TABLE 1

Ratios between Rate Constants (Obtained Individually), Reactivities, and Relative Adsorption Coefficients for the Pairs Phenylacetylene/Cyclohexene and Phenylacetylene/Styrene

Pair (A,B)	k_A/k_B	$R_{A,B}$[a]	$D_{A,B}$	$R_{A,B}$[b]	$D_{A,B}$[b]
PAC/CHE	1.83	269.1	147.1	—	—
PAC/STY	0.46	8.3	16.9	13.7	28.0
PAC/STY + 5×10^{-4} *M* Quinoline	1.12	11.0	9.8	25.6	22.8
STY/CHE[c]	4.02	32.4	8.1	—	—

Note: Reaction conditions: methanol solution of 0.46 *M* phenylacetylene in the individual reactions and 0.25 *M* in each substrate in the competitive reactions. Oveall volume, 20 ml; 0.01 g of catalyst $Pd_3PS_{400}(4)A$; 306 K; 0.414 MPa.

[a] $R_{A,B}$ and $D_{A,B}$ calculated from Eqs. (3) and (2), respectively.

[b] $R_{A,B}$ and $D_{A,B}$ calculated from Eqs. (4) and (2), respectively.

[c] $R_{A,B}$ calculated from the relation $R_{\text{STY/CHE}} = R_{\text{PAC,CHE}}/R_{\text{PAC,STY}}$ and $D_{A,B}$ calculated from Eq. (2). The presence of CHE and STY in the competitive reaction gives the same rate of PAC hydrogenation.

at the intersect of the product distribution profiles of the two substrates (Fig. 1) in the consecutive hydrogenation of phenylacetylene with liquid-phase molecular hydrogen; and (b) by using Eq. (4), proposed by Sporka *et al.* (*12*),

$$R_{A,B} = C_{B,\max}/C_{A,\max}, \qquad (4)$$

where $C_{B,\max}$ and $C_{A,\max}$ are the maximum styrene and phenylacetylene concentrations obtained from the above-mentioned product distribution profiles. The relative adsorption coefficients, $D_{A,B}$, were calculated from Eq. (2).

The reaction products were analyzed by gas chromatography, using high-purity standards for their characterization. Their nature was confirmed by mass spectrometry.

Diffusion was controlled by selecting the best shaking conditions and by using a support particle size of less than 0.140 mm. On the other hand, the application of the Koros-Novak criterion (*11*) allows us to state that our kinetic data were free from any influence of transport phenomena.

Figure 1A shows the product distribution profile for the phenylacetylene (PAC)/cyclohexene(CHE) pair, while Fig. 1B shows the graphical application of Eq. (1) to this pair. As can be seen from Fig. 1A, cyclohexene is not reduced as long as there is some phenylacetylene left in the medium and, when the latter disappears, both styrene and cyclohexene are reduced, the last at a lower reaction rate.

Table 1 reveals large differences between the adsorption coefficients of the phenylacetylene/cyclohexene and styrene/cyclohexene pairs, which accounts for the fact that phenylacetylene cannot be reduced by hydrogen transfer using cyclohexene as donor.

The addition of quinoline to the medium where the consecutive reduction of phenylacetylene was to take place decreased the aforesaid relative adsorption coefficients. We therefore added this amine to the reac-

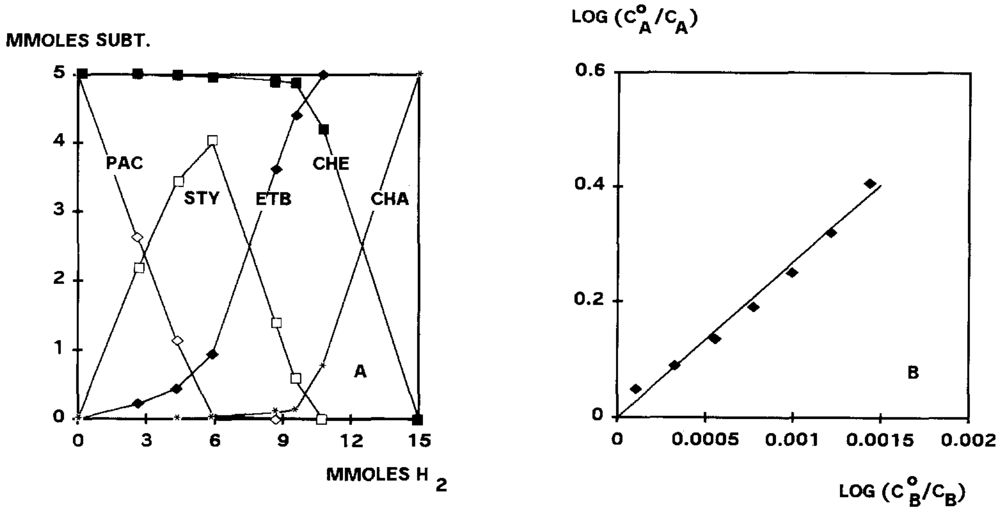

FIG. 1. (A) Variation in the distribution of reactants and products as a function of the extent of simultaneous hydrogenation of phenylacetylene/cyclohexene. (B) Logarithmic plot of the disappearance of phenylacetylene vs cyclohexene. For reaction conditions, see Table 1.

tion medium in the transfer reductions of phenylacetylene with cyclohexene as donor; however, the decrease in the relative phenylacetylene/cyclohexene adsorption coefficients was not sufficient to make the reaction feasible.

In summary, when a donor which is adsorbed at the same sites as the acceptor is used in hydrogen-transfer reactions, the adsorption of one of them—cyclohexene in our case—can be inhibited if the adsorption coefficients are very different and as a result the reaction will not take place.

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