

Competitive hydrogenation in alkene–alkyne–diene systems with palladium and platinum catalysts¹

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Abstract

Competitive hydrogenation of alkene, alkyne and diene substrates (C₆–C₈) over palladium and platinum catalysts were studied at 20°C and atmospheric pressure. Selectivities of these reactions were determined and the substrates relative adsorption coefficients calculated. It was found that hydrogenations of alkynic and dienic substrates were preferred in alkyne–alkene and diene–alkene systems, respectively. In these systems palladium catalyst selectivity was higher than selectivity of the platinum catalyst, due to higher relative adsorption coefficients of corresponding substrate couples on the palladium catalyst. © 1998 Elsevier Science B.V.

1. Introduction

The study of catalytic hydrogenation selectivity still remains amongst topical problems of modern heterogeneous catalysis [1–3]. In this work, the selectivities of competitive hydrogenation in alkyne–alkene, alkyne–diene, diene–alkene systems created by the opposite combination of selected model compounds (1-hexene, 1-heptene, 1-octene, 1-hexyne and 1,7-octadiene) were determined with palladium and platinum on active carbon in a methanolic solution. From these, with the use of initial reaction rate values of the individual hydrogenation of the model compounds, relative adsorption coefficients of individual substrates were calculated.

The acquired data were presented as part of the causal discussion of differed palladium and platinum catalyst selectivities.

2. Experimental

2.1. Chemicals

Substrates were of commercial origin (1-hexyne, 1-hexene, 1-heptene, 1-octene, 1,7-octadiene (Koch-Light, England)) and were distilled before use. Electrolytic hydrogen was used (ČSN 65 44 35, Linde-Technoplyn Praha). Methanol p.a. was used as a solvent (Penta, Chrudim). The catalyst 5% Pt/C ($S_{\text{BET}} = 1277 \text{ m}^2/\text{g}$) was prepared according to Červený et al. [4] and the fraction of grain size < 0.05 mm was used. The catalyst 3% Pd/C was commercial-Cherox 4100 ($S_{\text{BET}} = 1160 \text{ m}^2/\text{g}$) (Chem-

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opetrol, Litvínov) with Supersorbon Degussa HB-3 support and the catalyst grain size was < 0.02 mm.

2.2. Apparatus and kinetic measurements

Kinetic measurements were carried out using standard apparatus [5] at 20°C and atmospheric pressure; the hydrogenation rate was monitored by measuring the time-dependent hydrogen consumption and time-dependent changes of reactant concentrations detected by chromatographic analysis. 1 mmol of substrate was used in individual hydrogenation, where as 0.5 mmol of each substrate in 15 ml of methanol was used during competitive hydrogenations. The amount of catalyst ranged from 0.01–0.03 g.

2.3. Analytical methods

Samples were withdrawn in appropriately chosen time intervals and analyzed using a gas chromatograph Shimadzu GC-17A with flame ionization detector (FID) and capillary column J&W Scientific-DB5 ($30\text{ m} \times 0.32\text{ mm}$). In all cases, decane (Aldrich, USA) was used as an internal standard. Analyses were carried out at temperatures ranging between 55 – 150°C and at a split ratio of 1:50.

3. Results and discussion

All measurements were carried out in the kinetic regime. The external diffusion effect was eliminated by a sufficiently effective stir-

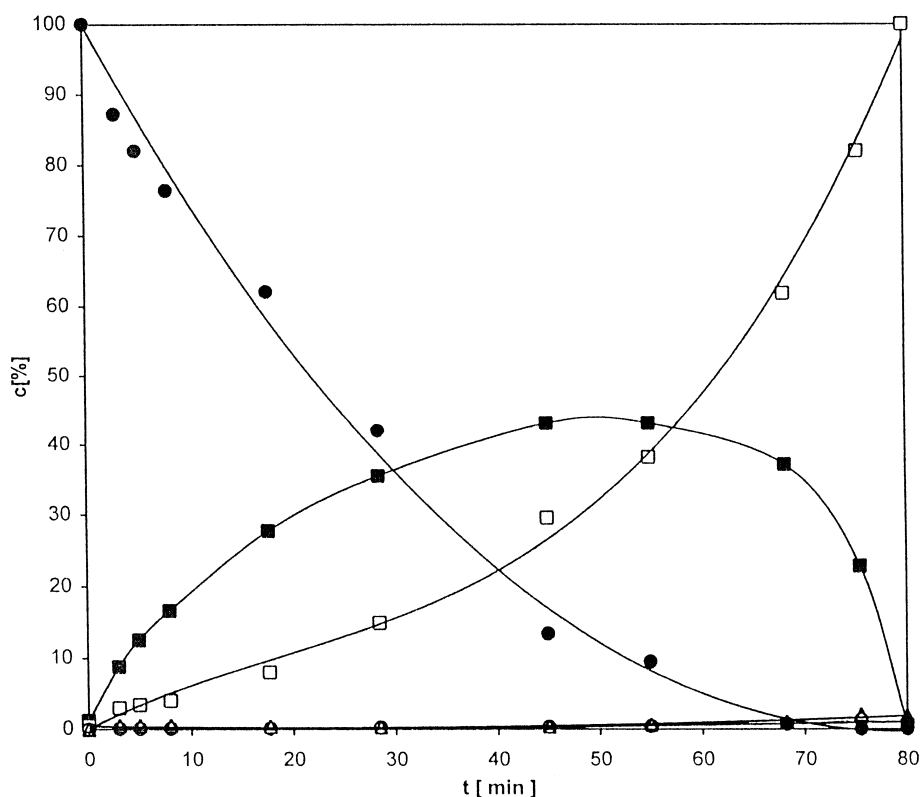


Fig. 1. Time dependence of concentrations of reactants and products during competitive hydrogenation of 1-hexyne on Pt/C in the system 1-hexyne–1-heptene. ●, 1-hexyne; ■, 1-hexene; ○, *cis*-2-hexene; △, *trans*-2-hexene and □, hexane.

ring, the pore diffusion effect was eliminated by the use of a sufficiently small catalyst grain.

From the measured dependence $c = f(t)$ for individual hydrogenations of chosen substrates, the initial reaction rate values were evaluated and afterwards employed for the calculation of the relative adsorption coefficients. The reactions were almost of a zero order to the substrates concentrations (also at high conversions).

The relative reactivities of the alkenic substrates (1-hexene, 1-heptene, 1-octene) evaluated from the hydrogenation of individual substrates and from competitive hydrogenation were comparable.

Figs. 1–4 show the typical course of 1-hexyne and 1-heptene competitive hydrogenations with platinum and palladium catalysts (c is the reaction component concentration related to the initial concentration of starting component in %, t

is time in min). As for lucidity each system is depicted in two figures.

It is apparent that using any of the two catalysts in the 1-hexyne–1-heptene system, the 1-hexyne hydrogenation was preferred while on the palladium catalyst the 1-hexyne hydrogenation was preferred more than on the platinum in comparison to the 1-heptene. From the comparison of Figs. 1, 2 and Figs. 3, 4 one can see that besides 1-hexyne hydrogenation also 1-heptene hydrogenation occurs from the start of the experiment. With the palladium catalyst 1-heptene hydrogenation did not occur with a remarkably higher velocity until 1-hexyne had disappeared from the reaction mixture. The 1-hexene concentration maximum aroused by 1-hexyne hydrogenation, was more conspicuous with the palladium catalyst than with the platinum one. Similar concentration dependencies were de-

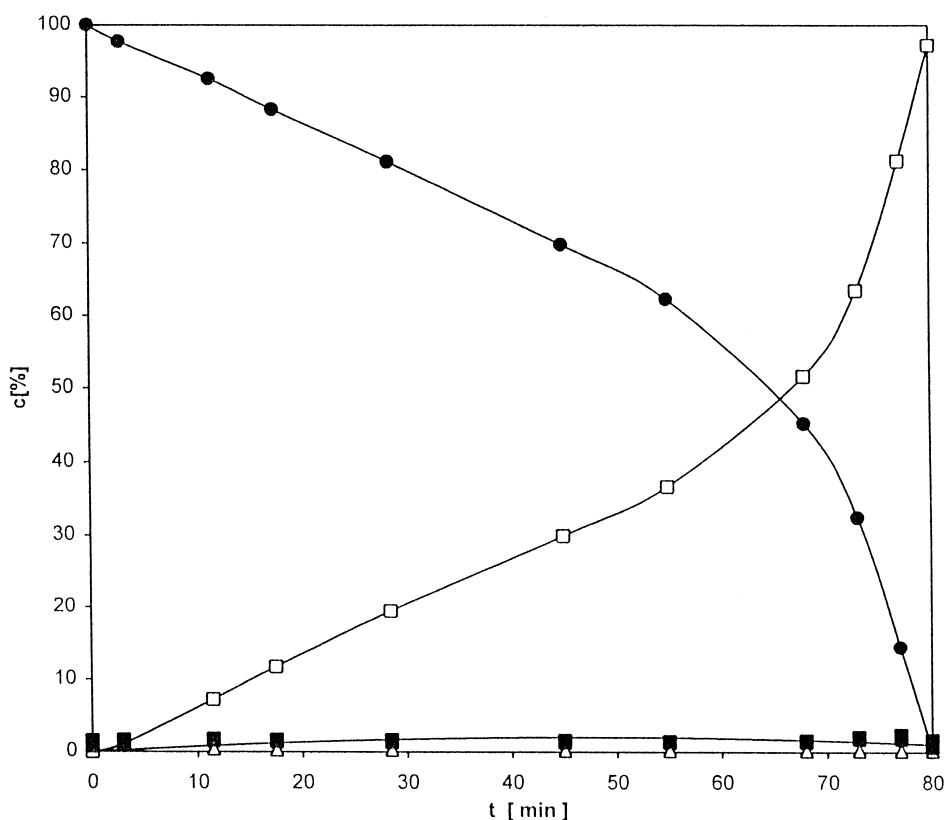


Fig. 2. Time dependence of concentrations of reactants and products during competitive hydrogenation of 1-heptene on Pt/C in the system 1-hexyne–1-heptene. ●, 1-heptene, △, *cis*-2-heptene; ■, *trans*-2-heptene and □, heptane.

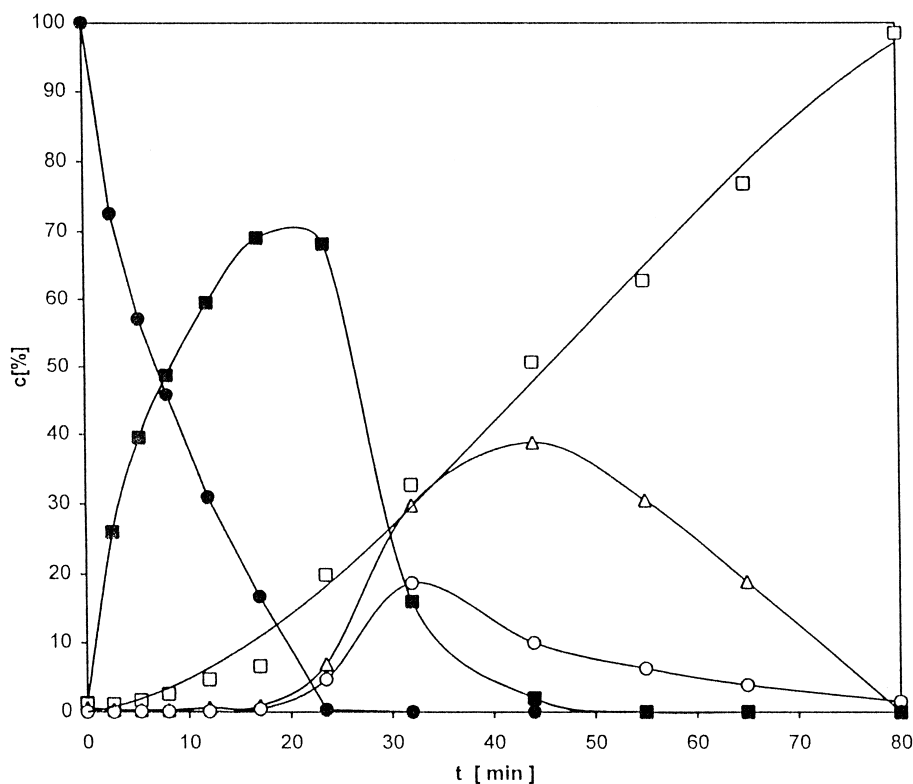


Fig. 3. Time dependence of concentrations of reactants and products during competitive hydrogenation of 1-hexyne on Pd/C in the system 1-hexyne–1-heptene. ●, 1-hexyne; ■, 1-hexene; ○, *cis*-2-hexene; △, *trans*-2-hexene and □, hexane.

tected with 1-hexyne–1-octene competitive hydrogenation.

Using the platinum catalyst, the reaction course was not exceedingly complicated by isomerization. When the model compounds were hydrogenated over a Pd/C catalyst a simultaneous double bond migration was observed (preferably from position 1 to a thermodynamically more stable position 2 in which, in addition, two isomers are possible). Differences between the palladium and platinum catalysts observed in this work are in good agreement with the observations of other authors [6–10].

1,7-Octadiene used as another model component, was competitively hydrogenated with 1-hexyne, 1-hexene and 1-heptene. 1,7-Octadiene hydrogenation coursed through 1-octene, which using the palladium catalyst partially isomerized to *cis* and *trans*-2-octene, which was further hydrogenated to octane.

A competitive hydrogenation selectivity may be expressed [11] by Rader–Smith Eq. (1):

$$S_{A,B} = \frac{r_A}{r_B} = \frac{k_A \cdot K_A}{k_B \cdot K_B} = \log \left(\frac{c_A}{c_A^0} \right) / \log \left(\frac{c_B}{c_B^0} \right) \quad (1)$$

where r = reaction rate, k = rate constant, K = adsorption coefficient, c = instantaneous concentration, c^0 = initial concentration and A and B designate compounds.

Eq. (1) is based on the assumption that the Langmuir–Hinshelwood types of kinetic equations describing individual substrate hydrogenation are identical.

The dependences measured were transformed to the Rader–Smith coordinates and from linear relations of the $\log(c_A/c_A^0)$ versus $\log(c_B/c_B^0)$

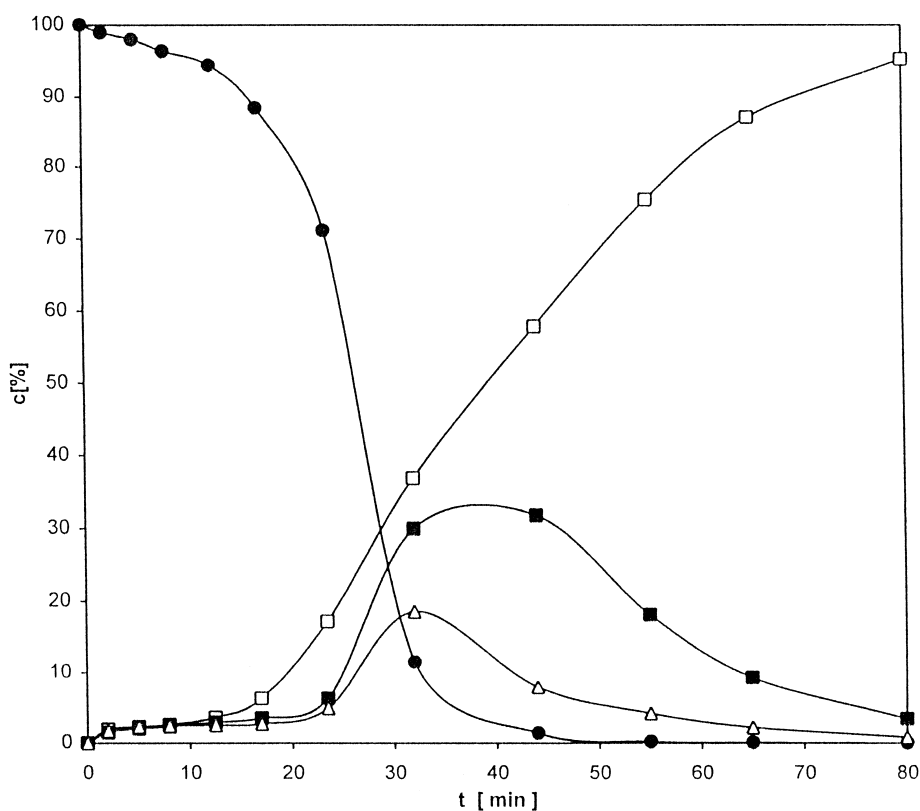


Fig. 4. Time dependence of concentrations of reactants and products during competitive hydrogenation of 1-heptene on Pd/C in the system 1-hexyne–1-heptene. ●, 1-heptene; △, *cis*-2-heptene; ■, *trans*-2-heptene and □, heptane.

curves described by Eq. (1). $S_{A,B}$ selectivity values were obtained (see Table 1).

Changes of the instantaneous concentrations of the starting compounds c_A and c_B includes

besides hydrogenation also alkene isomerisations.

Using the initial reaction rates in place of the rate constants k_A and k_B , relative adsorption

Table 1
Selectivities of competition reactions and adsorption coefficients

Substrate		$S_{A,B}$		k_A/k_B		K_A/K_B	
A	B	Pd	Pt	Pd	Pt	Pd	Pt
1-hexene	1-heptene	1.02	1.03	1.05	1.15	0.97	0.90
1-hexene	1-octene	0.98	1.04	1.00	1.22	0.98	0.85
1-heptene	1-octene	0.95	0.99	0.98	1.10	0.97	0.90
1-hexyne	1-octene	16.0	4.7	0.12	0.13	133.3	36.2
1-hexyne	1-heptene	15.0	4.7	0.13	0.15	115.4	31.3
1,7-octadiene	1-hexene	2.5	1.4	0.64	0.49	3.9	2.8
1,7-octadiene	1-heptene	2.4	1.8	0.67	0.53	3.6	3.4
1-hexyne	1,7-octadiene	6.5	3.0	0.19	0.28	34.2	10.7

coefficients K_A/K_B were calculated from the selectivity values; the data are given in Table 1. The following results were thus inferred:

Taken the experimental error into account $S_{A,B}$, r_A/r_B and K_A/K_B values measured in the different two component alkenic systems may well be considered equal, close to 1. In alkyne–alkene systems alkyne substrate was preferably hydrogenated with both catalysts. It was caused by its remarkably higher adsorption on the catalyst's surface (especially for Pd/C). However, during individual hydrogenations, alkene reacted more rapidly. $S_{A,B}$ value on the palladium catalyst was more than three times larger when compared to the Pt/C. Similarly, the relative adsorption coefficient was several times larger. However, the ratios of the two substrates rate constants (k_A , k_B) were approximately the same for both catalysts.

The preference of 1,7-octadiene hydrogenation in the diene–alkene system was again caused by a stronger diene adsorptivity, although, as an individual substrate, was hydrogenated slower than alkene. Relative diene/alkene adsorptivities for the palladium catalyst were somewhat higher than those for platinum.

In the case of competitive hydrogenation in the 1-hexyne–1,7-octadiene system using palladium and platinum catalysts, a higher alkyne reactivity was observed, again as a result of higher adsorptivity. On the contrary, during individual substrate hydrogenations, 1,7-octadiene was more reactive. Even in this system, there was a larger difference between alkyne and diene adsorptivity on palladium catalyst compared to the platinum one.

A possibility of a relative adsorption coeffi-

cients check-up was verified from independent measurements according [11] to Eq. (2):

$$K_{A,B} \cdot K_{B,C} \cdot K_{C,A} = 1 \quad (2)$$

where it is from definition inferred that:

$$K_{A,B} = \frac{1}{K_{B,A}} \quad (3)$$

In the olefin set (A = 1-hexene, B = 1-heptene, C = 1-octene) Eq. (2) was in good agreement with both catalysts. The pertaining product of adsorption coefficients for palladium and platinum catalysts were 0.96 and 0.95, respectively.

In a set of all three employed substances (A = 1-hexyne, B = 1-heptene, C = 1,7-octadiene), Eq. (2) was not as agreeable (0.94 for Pd, 0.86 for Pt), but still acceptable.

The provided findings imply a possibility to estimate the relative adsorption coefficients from the independently measured data for other substrates with unsaturated C–C bounds.

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