



# Coadsorption effect of the alkenic bond on the hydrogenation of the alkynic substrate on platinum and palladium catalysts

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## Abstract

Competitive catalytic hydrogenation of acetylenecarboxylic acid dimethylester, fumaric acid diethylester and maleic acid diethylester, respectively, were studied in liquid phase on palladium and platinum catalysts. Kinetic parameters evaluated from hydrogenation of individual substrates and of binary systems in competitive arrangements allowed a discussion of coadsorption effects of the alkenic bond on the reaction course of the alkynic substrate.

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**Keywords:** Competitive hydrogenation; Alkene–alkyne coadsorption; Adsorptivity; Palladium catalyst; Platinum catalyst

## 1. Introduction

A number of papers have been devoted to competitive hydrogenation of alkynic and alkenic bonds [1–4] and to the description of variations in their reactivities [3,4]. High selectivities of platinum and especially of palladium to the  $C\equiv C$  bond transformation could be attributed to a stronger adsorption of the  $C\equiv C$  bond on the catalytic surface compared to the  $C=C$  bond. In other words, the alkynic molecule replaces alkene from the surface and thus it is being hydrogenated only when certain surface coverage is attained. Under such circumstances only a limited area for monitoring the reactivity changes in the binary system of alkyne–alkene is available. To study reactivity variations it is necessary to find a system, in which the alkenic substance would demonstrate an adsorptivity

high enough to allow a competitive adsorption in the presence of the  $C\equiv C$  bond.

In this work, evaluation of the coadsorption effect of the alkenic bond on the course of hydrogenation of the alkynic substrate on palladium and platinum supported catalysts is presented. The effect of coadsorption was studied in the system of alkynic and alkenic esters of dicarboxylic acids. These molecules were expected to exhibit a strong interaction with the surface of the catalysts and also fulfil the assumption of the competitive adsorption of the  $C=C$  bond in the presence of the  $C\equiv C$  bond. The method of competitive hydrogenation was used to quantify this effect [1,2,5–11].

## 2. Experimental

### 2.1. Chemicals

Reactants—acetylenedicarboxylic acid dimethylester, fumaric acid dimethylester, maleic acid dimethylester, fumaric acid diethylester, maleic acid di-

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Table 1  
Characteristics of hydrogenation catalysts

Catalyst	Grain size (mm)	Particle size (nm)	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}_{\text{cat}}$ )	$S_{\text{MET}}$ ( $\text{m}^2_{\text{metal}}/\text{g}_{\text{cat}}$ )
3% Pd/C	<0.02	20.2	1160	32.8
5% Pt/C	<0.05	15.5	780	45.3

ethylester (Aldrich, USA). Propan-1-ol (Lachema, Czech Republic) was used as a solvent. Electrolytic hydrogen 4.0 (Linde Technoplyn, Czech Republic) was used.

## 2.2. Catalysts

The elemental crystallite size (XRD 3000, Co K $\alpha$  source of radiation, Rich Seifert & Co., Germany), the total surface area (BET N<sub>2</sub>/77 K, Pulse Chemisorb 2700, Micromeritics, USA) and the specific surface area of an active phase were chosen as characteristic features (Table 1) of the used catalysts—Pt/C-Secomet AN (Doducco Kat., GmbH), Pd/C-Cherox 4100ch (Chemopetrol a.s., Litvínov). The specific surface area of platinum was evaluated by the selective surface chemisorption of hydrogen followed by its potentiometric titration with oxygen. The same parameter for palladium was obtained by the selective chemisorption of CO assuming a surface ratio CO/Pd = 1/2. Platinum was characterised by 0 oxidation state, palladium catalyst was characterised after hydrogen activation as an aPdH-predominant phase with a low content of the bPdH phase.

## 2.3. Apparatus and kinetic measurement

Kinetic measurements were carried out isothermally in a semibatch stirred reactor [12] in the kinetic regime at 298 K and atmospheric hydrogen pressure in propan-1-ol. Reactions of individual substrates were monitored by measuring time dependencies of hydrogen consumption and of concentration changes of the substances presented in the reaction mixture (GLC). Typically, 0.25–1 mmol of a substrate in 15 ml of propan-1-ol was used. The amount of platinum catalyst introduced to the kinetic experiment was 0.07 and 0.01 g for the palladium catalyst. Competitive hydrogenations in binary systems were carried out with

the molar ratio of the substrates 1:1, if not mentioned otherwise.

## 2.4. Analytical methods

Samples of reaction mixtures were analysed on GLC Varian 3800 (Varian, USA) equipped with flame-ionisation detector and capillary column VA-WAX (60 m  $\times$  0.25 mm  $\times$  0.25 mm; Varian, USA) using temperature program ranging between 333 and 453 K and the overpressure of carrier gas (N<sub>2</sub>) 80 kPa. The composition of the reaction mixture was determined using the internal standard method (*n*-decane, Aldrich, USA).

## 3. Results and discussion

### 3.1. Hydrogenation of model alkenes

Alkenic substrates with different geometric arrangements on the C=C bond (*cis*, *trans*) and the size of esteric alkyl (methyl, ethyl) were hydrogenated. Measured time dependencies of reactant concentrations were used for determination of initial reaction rate values. In the majority of experiment, the reactions were of zero order to the concentration of substrates up to high conversions (>90%). All hydrogenations proceeded with total conversion of substrate according to the scheme A  $\rightarrow$  B. These values ( $r_{0\text{C}=\text{C}}$ ) are given in Table 2. Esters with the *cis* arrangement on the C=C bond were more reactive compared to the esters with the *trans* arrangement on the C=C bond. In hydrogenation of maleic acid esters, no products of isomerisation were observed (i.e. fumaric acid

Table 2  
Initial hydrogenation rates of model alkenic substrates

Catalyst	Substrate	$r_{0\text{C}=\text{C}}$ (mmol/(min g <sub>cat</sub> ))
Pd/C	Dimethylester of maleic acid	17.9 $\pm$ 0.4
	Diethylester of maleic acid	15.9 $\pm$ 0.3
	Dimethylester of fumaric acid	2.6 $\pm$ 0.1
	Diethylester fumaric acid	2.5 $\pm$ 0.1
Pt/C	Dimethylester of maleic acid	1.73 $\pm$ 0.04
	Diethylester of maleic acid	1.67 $\pm$ 0.03
	Dimethylester of fumaric acid	0.59 $\pm$ 0.03
	Diethylester of fumaric acid	0.54 $\pm$ 0.03

esters and vice versa). The size of their alkyl substituent had rather a negligible effect upon the surface reaction rate, nevertheless, ethylester was always less reactive compared to methylester.

### 3.2. Hydrogenation of model alkyne on palladium catalyst

The hydrogenation course of acetylenedicarboxylic acid dimethylester on palladium catalyst is shown in

Fig. 1. The hydrogenation of the alkyne bond was preferred to the transformation of the alkenic bond of the reaction intermediate due to the stronger adsorption of the  $C\equiv C$  bond on the catalytic surface compared to the  $C=C$  bond. Regardless of this well-known phenomenon, it was apparent that in respect to the production of the  $C=C$  bond, palladium catalyst did not exhibit the selectivity high enough to completely separate the two consecutive reactions ( $A \rightarrow B$  and  $B \rightarrow C$ ). However, the product of the total hydrogenation

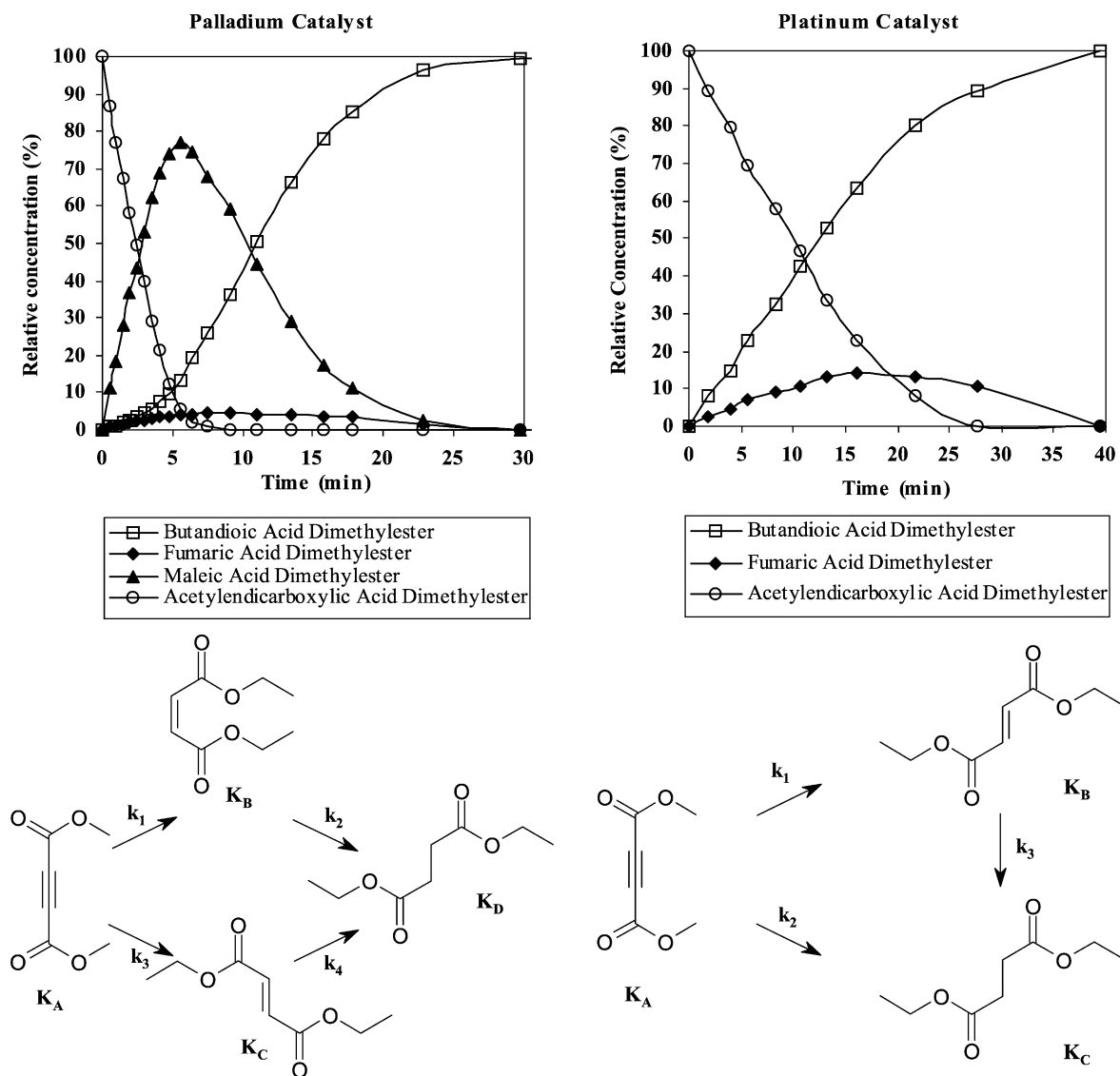


Fig. 1. Hydrogenation course of acetylenedicarboxylic acid dimethylester on palladium and platinum catalysts.

Table 3

Results of hydrogenations of acetylenecarboxylic acid dimethylester and fumaric and maleic acid dimethylesters

$r_{0C\equiv C}$	$r_{C=C}$ (mmol/(min g <sub>cat</sub> ))	$r_{0C=C}$ (mmol/(min g <sub>cat</sub> ))	$S_{\max,C=C}$ (%)	$c_{C=C\max.}$ (%)
Palladium catalyst				
21.3 ± 0.5	0.2 ± 0.1 (F) 3.6 ± 0.4 (M)	2.6 ± 0.1 (F) 17.9 ± 0.4 (M)	95	85
Platinum catalyst				
0.76 ± 0.03	0.55 ± 0.05 (F) x (M)	0.59 ± 0.03 (F) 1.73 ± 0.04 (M)	26	13

F, fumaric acid dimethylester; M, maleic acid dimethylester. x—M was not presented in reaction mixture during hydrogenation of acetylenecarboxylic acid.

of the C≡C bond (alkyne) was present in the reaction mixture from the very early stages. This behaviour of palladium could be attributed to the structure of the catalyst used. Palladium catalyst showed a high value of the active metal particle size and the presence of the bPdH phase. Apparently, this resulted in a competitive adsorption and hydrogenation of the C=C bond in the presence of the C≡C bond [13]. Probably also the structure of the hydrogenated substrate and the produced alkenic intermediate had a significant influence upon the not very selective hydrogenation course of C≡C bond to C=C bond. Hydrogenation of acetylenedicarboxylic acid dimethylester proceeded according to the scheme shown in Fig. 1. Isomerisation of alkenic intermediates did not proceed from the bulk phase as proved in hydrogenations of individual esters of fumaric and maleic acids. Table 3 involves parameters characterising hydrogenation course of the model alkyne substance (values of the initial reaction rates ( $r_0$ ), rates of the consecutive reaction of alkenic intermediate ( $r_{C=C}$ ) after disappearance of all alkyne from a reaction mixture). The hydrogenation selectivity in respect to the production of the alkenic intermediate ( $S_{\max,C=C}$ ) was defined as a ratio of instantaneous concentration of alkene (the sum of esters of fumaric and maleic acid) and conversion of the starting substance and it was characterised by the maximum achieved value of this quantity during the reaction. The dependence  $S_{\max,C=C}$  upon conversion was always identical, whereas already at low conversions (<5%), this quantity reached its maximum value (constant up to high conversion values >80%). Consecutively, its value decreased along the significant decrease of the ratio alkyne:alkene and the occupancy changes on the catalytic surface. The values of the highest achieved concentration of the alkenic sub-

strate in the reaction mixture ( $c_{C=C\max.}$ ) characterised also the selective courses of hydrogenation.

Hydrogenation course (Fig. 1) of acetylenedicarboxylic acid dimethylester on palladium catalyst was described by the following kinetic equations of the Langmuir–Hinshelwood type:

$$r_1 = \frac{k_1 c_A}{c_A + c_B K_B^{\text{rel}} + c_C K_C^{\text{rel}} + c_D K_D^{\text{rel}}}$$

$$r_2 = \frac{k_2 c_A}{c_A + c_B K_B^{\text{rel}} + c_C K_C^{\text{rel}} + c_D K_D^{\text{rel}}}$$

$$r_3 = \frac{k_3 c_B K_B^{\text{rel}}}{c_A + c_B K_B^{\text{rel}} + c_C K_C^{\text{rel}} + c_D K_D^{\text{rel}}}$$

$$r_4 = \frac{k_4 c_C K_C^{\text{rel}}}{c_A + c_B K_B^{\text{rel}} + c_C K_C^{\text{rel}} + c_D K_D^{\text{rel}}}$$

$$K_B^{\text{rel}} = \frac{K_B}{K_A}$$

$$K_C^{\text{rel}} = \frac{K_C}{K_A}$$

$$K_D^{\text{rel}} = \frac{K_D}{K_A}, \quad \text{while } K_D = 0$$

The reaction scheme (Fig. 1) was simplified by neglecting the isomerisation equilibrium between dimethylesters of fumaric and maleic acid (not proved). Table 4 presents the results in a form of values of rate constants and adsorption constants. Strong adsorption of the C≡C bond compared to the C=C reveals, while the *trans*-isomer—dimethylester of fumaric acid—adsorbed much less on the catalyst surface than the *cis*-isomer—dimethylester of maleic acid.

Table 4

Parameters of kinetic equations of acetylenedicarboxylic acid dimethylester hydrogenation on palladium and platinum catalysts

Rate constant ( $\text{mol dm}^{-3} \text{g}_{\text{cat}}^{-1}$ )				Adsorption coefficient		
$k_1$	$k_2$	$k_3$	$k_4$	$K_A$	$K_B$	$K_C$
Palladium catalyst						
$0.23 \pm 0.02$	$0.010 \pm 0.001$	$0.11 \pm 0.01$	$0.11 \pm 0.03$	$19.9 \pm 0.4$	$3.7 \pm 0.4$	$1.1 \pm 0.3$
Platinum catalyst						
$0.020 \pm 0.02$	$0.050 \pm 0.003$	$0.06 \pm 0.01$	–	$4.9 \pm 0.4$	$2.6 \pm 0.2$	–

In parallel the exponential kinetic model was also used. Zero reaction order to acetylenedicarboxylic acid dimethylester was determined based on the independence of the reaction rate on the initial concentration of this substrate (first order related to hydrogen was also proved by a separate series of experiments). At the point corresponding approximately to 80%-conversion, the change in the reaction order occurred. The area of higher conversions (above 80%) could be satisfactorily described by exponential kinetics of first order related to acetylenedicarboxylic acid dimethylester. This behaviour—the change of the reaction order related to the alkyne substrate during the hydrogenation course, could be attributed to the decrease of the ratio alkyne/catalyst, which resulted in the incomplete catalyst surface occupancy, by the alkyne substrate [3–5]. Separate experiments (the initial concentration of the alkyne model substance was decreased to a level corresponding to the ratio alkyne/catalyst at 80%-conversion in the original experiment) proved that the ratio alkyne/catalyst did not initiate such behaviour. The change of the order occurred identically in the original experiment approximately at 80%-conversion. At the point corresponding to 80%-conversion, the ratio alkyne:alkene was approximately 3:1. Having carried out an experiment with the initial composition corresponding to the above-mentioned conversion of acetylenedicarboxylic acid dimethylester, the time dependence of alkyne concentration was acquired. This was identical to the original experiment at the conversion higher than 80%, i.e. the first order related to the alkyne substrate. Therefore, it was apparent that the order alteration, related to the alkyne substrate, was initiated by an increase of the alkene concentration in the reaction mixture to a level sufficiently high to allow a change in the adsorption behaviour of alkyne (macro-

scopically demonstrated by the change of order, related to this substance). Behaviour of alkenic intermediates was also affected by specific interactions on the catalytic surface. From the macroscopic view, these interactions were demonstrated by a decrease of hydrogenation rate of the C=C bond after hydrogenation of the alkyne substrate ( $r_{\text{C=C}}$ ) in comparison to hydrogenations of alkenic model substances as individuals ( $r_{\text{C=C0}}$ ) (Table 3). The decrease of the Pd/C activity to hydrogenation of alkenes (after carrying out hydrogenation of alkyne) was reversible, i.e. after the treatment of Pd/C with hydrogen the catalyst exhibited the original activity to the alkene hydrogenation. A speculative explanation could be based on the reduction of an effective amount of the surface hydrogen on palladium [3] hydrogen present in the palladium lattice (occluded hydrogen) consumed for hydrogenation of the C≡C bond [14], respectively.

### 3.3. Hydrogenation of model alkyne on platinum catalyst

Hydrogenation course of the model alkyne substance—acetylenedicarboxylic acid dimethylester—on platinum catalyst is shown also in Fig. 1. The reaction course was markedly different from hydrogenation of this substrate on palladium catalyst. The reaction proceeded according to the scheme shown in Fig. 2. From the alkenic intermediates, only fumaric acid dimethylester was detected in relatively low concentration levels (<20%), whereas maleic acid dimethylester probably remained in the adsorbed state and consequently reacted to the saturated product—butanedioic acid dimethylester. Table 3 shows parameters characterising the hydrogenation course of alkyne model substances on Pt/C. The value  $r_{\text{C=C}}$  (only fumaric acid dimethylester was presented in

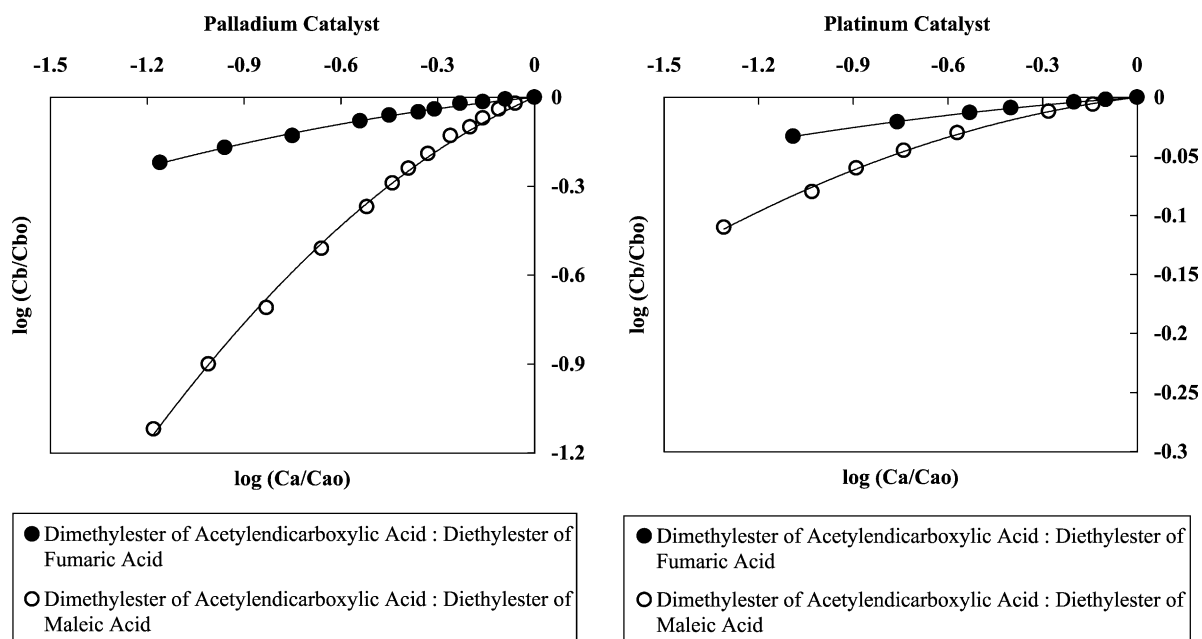


Fig. 2. The course of competitive hydrogenation of alkyne:alkene on palladium and platinum catalysts.

the bulk phase) did not differ significantly from the value  $r_{C=C0}$  on the platinum catalyst (compared to palladium catalyst).

The hydrogenation course (Fig. 1) of acetylenedicarboxylic acid dimethylester on platinum catalyst was described again by the kinetic equations of the Langmuir–Hinshelwood type:

$$r_1 = \frac{k_1 c_A}{c_A + c_B K_B^{\text{rel}} + c_C K_C^{\text{rel}}}$$

$$r_2 = \frac{k_2 c_A}{c_A + c_B K_B^{\text{rel}} + c_C K_C^{\text{rel}}}$$

$$r_3 = \frac{k_3 c_B K_B^{\text{rel}}}{c_A + c_B K_B^{\text{rel}} + c_C K_C^{\text{rel}}}$$

$$K_B^{\text{rel}} = \frac{K_B}{K_A}$$

$$K_C^{\text{rel}} = \frac{K_C}{K_A}, \quad \text{while } K_C = 0$$

The scheme on Fig. 1 outlined the reaction from alkyne directly to alkane. It probably proceeded through the intermediate state of maleic acid dimethylester (no occurrence of its desorption to the bulk phase). Table 4

shows the results in a form of values of rate constants and adsorption coefficients.

Similarly to the palladium catalyst, it was proved that the reaction order alteration, related to the alkyne substrate, was likely caused not by the low ratio of alkyne/catalyst, but by the increasing ratio of alkene:alkyne.

### 3.4. Competitive hydrogenation of alkene:alkyne

The method of competitive hydrogenation, in which two or more substances react in the same time—compete for an active site—represents a significant tool to study adsorption under reaction conditions and it is suitable for evaluation of the interaction between a catalyst and a substrate. For competitive reaction of two substances with kinetics that can be expressed by rate equations of identical forms, it is possible to obtain a relatively simple equation for selectivity. It is defined by the ratio of both substances, known the Rader–Smith equation [11]:

$$\frac{\log(c_A/c_{A0})}{\log(c_B/c_{B0})} = \frac{k_{\text{AH}} K_A}{k_{\text{BH}} K_B} = S_{\text{AB}} \quad (1)$$

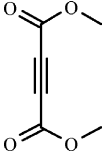
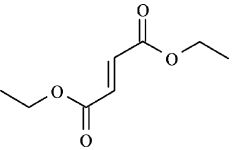
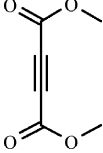
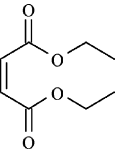
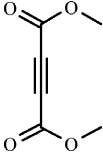
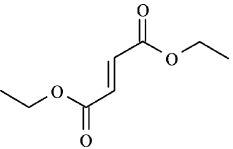
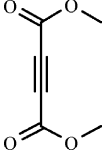
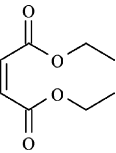
Ideally, the dependence  $\log(c_A/c_{A0})$  upon  $\log(c_B/c_{B0})$  is graphically expressed by the slope of a straight line  $S_{AB}$ . Using the initial reaction rates of hydrogenations of individual substrates  $r_0$  to replace the values of rate constants  $k_{AH}$  and  $k_{BH}$  in Eq. (1) and introducing the acquired value of selectivity  $S_{AB}$  to this equation, relative adsorption coefficient  $K_A/K_B$  can be obtained.

Competitive hydrogenations in binary systems of acetylenedicarboxylic acid dimethylester (substrate A): alternative maleic or fumaric acid diethylester (substrate B) were carried out. Ethylesters instead of methylesters were used as the model alkenic substances to distinguish the behaviour of alkene in the process of production in the reaction mixture from alkene introduced to the competitive hydrogenation. Separate experiments demonstrated minimal differences in reactivities of methylester of alkenic dicarboxylic acid and ethylester of the identical acid. Fig. 2 shows the results of competitive hydrogenation, where the courses of competitive hydrogenations are depicted in the Rader–Smith coordinates. It is apparent (Fig. 2) that the binary systems alkyne/alkene manifested significant deviations from the linearity of the Rader–Smith equation, i.e. the reactivity value, represented in the binary system of alkyne/alkene by the parameter of selectivity of competitive hydrogenation decreased during the reaction course in the sense of a continuously decreasing reactivity of an alkynic substrate. This fact corresponded with the above-verified phenomenon of the reaction order change in relation to an alkynic substrate as a reason of the presence of alkenic substance and the consecutive effects of surface processes on the catalyst. Since the order change in relation to an alkynic substrate was demonstrated no earlier than at higher conversion of alkyne—approximately at 80%-conversion (the ratio of alkyne:alkene, 1:3), it is apparent (Fig. 2) that the  $C\equiv C$  bond reactivity is gradually affected by the presence of the  $C=C$  bond, while this process starts at very low concentration of alkene in the reaction mixture. This fact is apparent from the values of selectivities of competitive hydrogenations at 25, 50, 75 and 95%—conversion of alkyne ( $S'_{AB25}$ ,  $S'_{AB50}$ ,  $S'_{AB75}$ ,  $S'_{AB95}$ ) acquired from the competitive hydrogenations that were carried out using various starting ratios of alkyne:alkene and are presented in Table 5. These quantities are not in fact, real

selectivities of competitive hydrogenations, however expressing only the instantaneous state of this quantity corresponding to the particular conversion of alkyne. Values of these quantities manifested an identical trend with both experimentally verified catalysts and decreased with an increasing conversion of alkyne. If certain assumptions are fulfilled, the method of competitive hydrogenation allows to separate the surface reaction rates of individual competitively reacting substances—the parameter of the relative reactivity—from their adsorption behaviours—the parameter of the relative adsorptivity. The values of the surface reaction rates were acquired based on the assumption of total occupancy of active centres of a catalyst by a hydrogenated substrate from the reactions of model substances in individual arrangements. If the assumption of a constant value of the parameter of the relative reactivity, acquired by the above-described method, was applied, the non-linearity of the Rader–Smith equation could be associated with the parameter of the relative adsorptivity. If the assumption of a constant value of the relative reactivity were fulfilled, the curves in the Rader–Smith coordinates would have to coalesce to one curve for different starting ratios of alkyne:alkene after adjusting to an identical starting status, i.e. to the ratio of alkyne:alkene, 1:1. This assumption was fulfilled in the case of platinum catalyst. On the palladium catalyst, the behaviour of the binary mixtures with variable ratios of alkyne:alkene was different in dependence on time during which alkynic substrate reacted on the catalytic surface. The longer was the reaction time of the competitive hydrogenation with various ratios of alkyne:alkene for achieving the identical composition of the reaction mixture, i.e. the ratio alkyne:alkene (the sum of alkenes), the higher was the selectivity value of the competitive reaction. This fact was probably associated with the decrease of hydrogenation rate of alkenic substance after alkyne was eliminated from the reaction mixture, i.e. after eliminating the difference in values of the parameters  $r_{C=C0}$  and  $r_{C=C}$ . This fact was reasoned above as a decrease of the effective amount of the surface hydrogen on palladium, hydrogen consumption present in the palladium lattice—occluded hydrogen—necessary for hydrogenation of the  $C\equiv C$  bond, respectively, while its absence consecutively caused a decrease of the hydrogenation rate of the alkenic substrate.

Table 5

Values of selectivities of competitive hydrogenations for various starting ratios of alkyne/alkene on palladium and platinum catalysts

Substrate		Molar ratio	Selectivity of competitive hydrogenation			
A	B	A:B	$S'_{AB25}$	$S'_{AB50}$	$S'_{AB75}$	$S'_{AB95}$
Palladium catalyst						
		3:1	143	83	56	52
		1:1	53	45	40	34
		1:3	33	28	20	14
		3:1	50	31	22	17
		1:1	24	22	19	12
		1:3	10	7	5	2
Platinum catalyst						
		3:1	20	12	9	7
		1:1	9	7	6	5
		1:3	6	5	4	3
		3:1	5	4	3	2
		1:1	2.0	1.5	1.3	1.2
		1:3	1.3	1.1	1	0.9

#### 4. Conclusion

It was proved that the process of competitive hydrogenation of the alkenic and alkynic bond proceeded on supported palladium and platinum catalysts with a continuous change of reactivity in dependence to the change of the ratio alkyne:alkene. On platinum catalyst, it was possible to attribute such behaviour to continuously changing adsorption behaviour of the alkenic and alkynic substrate. On palladium catalyst an extra parameter—a change of surface reactions—occurred probably as a result of a decrease of the effective amount of surface hydrogen.

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