

The influence of cycloalkylsubstituent on the hydrogenation of terminal alkynic and alkenic bonds on platinum and palladium catalysts

Petr Kačer, Libor Červený*

Department of Organic Technology, Institute of Chemical Technology, ICT Prague Technická 5, 16628 Prague 6; Czech Republic

Received 12 July 2003; received in revised form 11 September 2003; accepted 17 October 2003

Abstract

The work is concerned with structure effects exerted by molecules of substituted acetylenes and ethylenes (cyclopropyl, cyclopentyl, cyclohexyl, phenyl) in heterogeneously catalyzed hydrogenation on platinum and palladium supported catalysts. Kinetic parameters, acquired from hydrogenation of individual model substances as well as binary systems in competitive arrangements enabled discussion of structural effects in heterogeneously catalysed hydrogenation. The method of competitive hydrogenation allowed the assessment of the relation between the molecular structure and the rate of a surface reaction in parallel with the stability of the surface complex.

© 2003 Published by Elsevier B.V.

Keywords: Adsorptivity; Competitive hydrogenation; Molecular structure effects; Substituent effects

1. Introduction

The number of papers studying molecular structure effects of alkynic compounds on the course of heterogeneously catalysed hydrogenation is rather limited. This fact is amazing especially when compared to the number of existing articles involving the similar topic in the field of alkenic substrates [1–4]. Acetylene has been the most intensively studied substrate of this family in the past. However, it was evidenced by Jackson and co-workers [5,6], that extension of kinetic and mechanistic theories from acetylene hydrogenations to other alkynic substrates can be recommended only with precautions, because alkynic transformations (especially on palladium catalysts) were structure sensitive.

This work evaluates the effects of cyclic substituents (cyclopropyl, cyclopentyl, cyclohexyl, and phenyl) on the course of hydrogenation of the terminal alkynic bond. The acquired results were compared to the effects of similar substituents on the terminal alkenic bond. The method of competitive hydrogenation enabled to evaluate effects

of these structural units on the surface reaction rate and stability of the adsorbed complex [1–3,7–10].

2. Experimental

2.1. Chemicals

All reactants—cyclopropylacetylene (VÚOS Pardubice, Czech Republic), cyclopentylacetylene, cyclohexylacetylene, cyclopropylethylene (DOT-ICT Prague, Czech Republic), phenylacetylene, styrene, cyclopentylethylene and cyclohexylethylene (Aldrich, USA)—were freshly distilled before use. Reactions were carried out in a solvent—methanol p.a. (Penta, Czech Republic). Electrolytic hydrogen 4.0 (Linde Technoplyn, Czech Republic) was used.

2.2. Catalysts

The elemental crystallite size (XRD 3000, Co K α source of radiation, Rich. Seifert & Co., Germany), the total surface area (BET N₂/77 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 (Doduco Kat. GmbH, Germany),

* Corresponding author. Tel.: +42-2-24-35-42-14; fax: +42-2-24-31-19-68.

E-mail addresses: kacerp@vscht.cz (P. Kačer), cervenyl@vscht.cz (L. Červený).

Table 1
Characteristics of hydrogenation catalysts

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

Pd/C-Cherox 4100ch (Chemopetrol, Czech Republic). 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 $\text{CO}/\text{Pd} = 1/2$. Platinum was characterised by 0 oxidation state, palladium catalyst was characterised after hydrogen activation as an αPdH -predominant phase with a low content of the βPdH phase.

2.3. Apparatus and kinetic measurement

Kinetic measurements were carried out in a semi-batch stirred reactor isothermally at 298 K and atmospheric hydrogen pressure. All measurements were carried out in the kinetic region. Hydrogenation courses of individual substrates were monitored by measuring time changes of concentrations of substances in the reaction mixture. These values were determined using chromatographic analysis (GLC). Typically 1 mmol of a substrate in 15 ml of methanol was used. The amount of platinum catalyst introduced to the kinetic experiment was 0.01 and 0.005 g for palladium catalyst. Competitive hydrogenations in binary systems were carried out with 0.5 mmol of each substrate.

2.4. Analytical methods

Samples withdrawn in selected time intervals were analysed on the gas chromatograph Varian 3800 (Varian, USA) equipped with flame-ionisation detector and capillary column VA-WAX—length 60 m, i.d. 0.25 mm, film thickness of stationary phase 0.25 μm (Varian, USA) using temperature program ranging between 333 and 453 K and the overpressure of carrier gas (N_2) 80 kPa. The composition of the reaction mixture was determined by using the internal standard method (*n*-decane, Aldrich, USA).

3. Results and discussion

3.1. Hydrogenation of model alkynes

Hydrogenations of acetylenic substrates differing in their substituent—hydrocarbonic ring (cyclopropyl, cyclopentyl, cyclohexyl, phenyl)—located on a triple bond were carried out. Figs. 1 and 2 show the hydrogenation courses of model alkynic substances on platinum and palladium catalysts as

well as a proposed reaction scheme. It is apparent that hydrogenation of cyclohexyl- and phenylacetylene proceeded on both catalysts according to the formal reaction scheme as consecutive reactions ($\text{A} \rightarrow \text{B} \rightarrow \text{C}$). In the case of cyclopropyl- and cyclopentylacetylene, a formal reaction scheme of a parallel-consecutive reaction was applied, which was caused by hydrogenolytic reactions proceeding on these rings parallel to the hydrogenation of relevant ethylenic intermediates. In all cases, hydrogenation of the alkynic bond was preferred to the alkenic bond transformation of a reactive intermediate (a stronger adsorption of $\text{C}\equiv\text{C}$ bond on a catalytic surface compared to $\text{C}=\text{C}$ bond). After a complete elimination of an alkynic substrate from the reaction mixture, hydrogenation rate significantly increased due to the occupation of the vacant catalytic surface (previously occupied by an alkynic substrate) by an alkenic intermediate with a significantly higher value of the surface reaction rate (compared to the relevant alkyne).

On comparison hydrogenation of individual alkynic substrate on both catalysts, palladium manifested higher selectivity toward the double bond formation. In hydrogenation of cycloalkylacetylenic substrates on the palladium catalyst, up to high conversions, an entire separation of the first reaction step ($\text{A} \rightarrow \text{B}$) from the consecutive reactions of an alkenic intermediate ($\text{B} \rightarrow \text{C}$) was feasible. Hydrogenation of phenylacetylene was an exception, especially when compared to cyclohexylacetylene (identical reaction scheme $\text{A} \rightarrow \text{B} \rightarrow \text{C}$). Contrary to the hydrogenation of cyclohexylacetylene, in which the palladium catalyst showed high enough selectivity to allow separation of the two consecutive steps ($\text{A} \rightarrow \text{B}$ and $\text{B} \rightarrow \text{C}$), in the case of phenylacetylene, ethylbenzene was present in the reaction mixture from the very beginning. Palladium catalyst was not sufficiently selective for hydrogenation of phenylacetylene to styrene, which could be explained in association with the structure of the catalyst used (i.e., showing a high value of the average active metal particle size and the presence of the βPdH phase) [11]. Most likely it could be effected by aromatic ring moiety. In hydrogenation of substituted acetylenes on the platinum catalyst always (even at low conversions) certain amount of alkanic product was indicated. Such behaviour of the platinum catalyst could be attributed either the competitive adsorption of the alkenic product (even at very high ratios of alkyne/alkene) or to the fact that it remained in an adsorbed state and reacted further to the corresponding alkane. Also a combination of the two mechanisms could be assumed.

Hydrogenation of all model alkynic substances on both catalysts were, up to high conversions, of zero order to an alkynic substrate and were carried out with total conversions. Table 2 shows parameters characterising the hydrogenation course of individual alkynic substrates on palladium and platinum catalyst. Using linear areas from the concentration dependence of an acetylenic substrate on time, values of initial reaction rates (r_0) were evaluated. These were used for the calculation of the relative adsorption coefficients

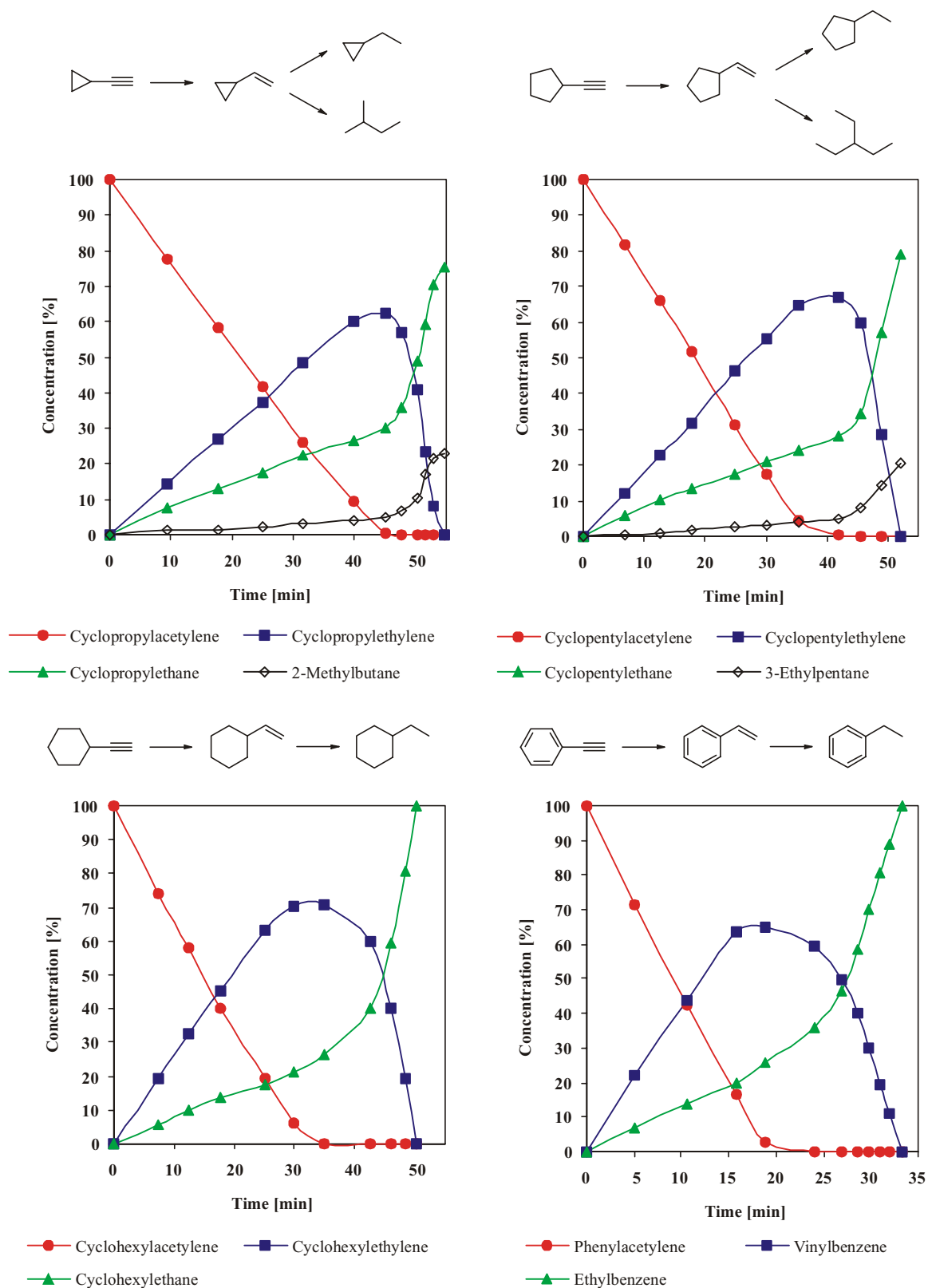


Fig. 1. Hydrogenation course of substituted alkynes on platinum catalyst.

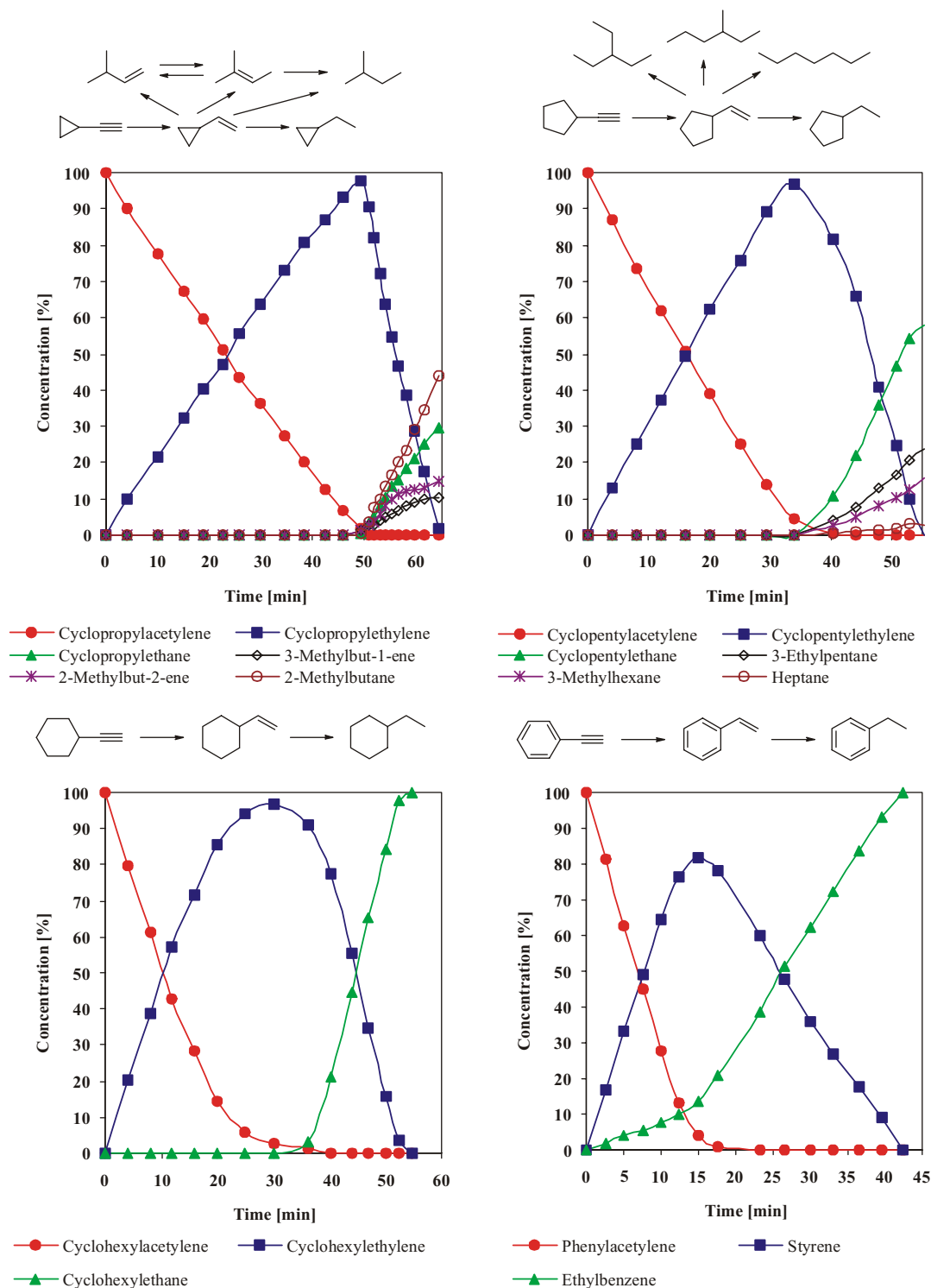


Fig. 2. Hydrogenation course of substituted alkynes on palladium catalyst.

using the Rader–Smith equation [7]. The rates of consecutive reactions of an alkenic intermediate ($r_{C=C}$) were evaluated after a complete elimination of all alkyne from the relevant reaction mixture in the same way as r_0 values. Hydrogenation of individual substrates were carried out under different temperatures (288, 298, 308, and 318 K), based on

which the values of apparent activation energies were calculated. The values ranged between 36 and 43 kJ mol⁻¹ on Pt/C and 26–30 kJ mol⁻¹ on Pd/C. The selectivity of hydrogenation, related to the production of an alkenic intermediate ($S_{\max,C=C}$), was defined as a ratio of instantaneous concentration of the substituted alkene and the conversion

Table 2
Results of hydrogenations of substituted acetylenes (individual arrangement)

Substrate	r_0 (mmol min ⁻¹ g _{cat} ⁻¹)	$r_{C=C}$ (mmol min ⁻¹ g _{cat} ⁻¹)	E_A (kJ mol ⁻¹)	$S_{\max, C=C}$ (%)	$c_{C=C\max}$ (%)	$c_{H\text{-lysis}}$ (%)
Platinum catalyst						
Cyclopropylacetylene	2.8 ± 0.1	12.3 ± 0.5	42.7 ± 0.4	77	63	26
Cyclopentylacetylene	3.7 ± 0.1	10.1 ± 0.3	40.6 ± 0.9	72	67	20
Cyclohexylacetylene	4.8 ± 0.1	9.5 ± 0.2	39.2 ± 0.5	82	71	0
Phenylacetylene	5.8 ± 0.1	8.6 ± 0.2	36.6 ± 0.8	74	65	0
Palladium catalyst						
Cyclopropylacetylene	4.1 ± 0.1	14.1 ± 0.5	29.8 ± 0.8	>99.9	97	71
Cyclopentylacetylene	6.4 ± 0.1	13.0 ± 0.5	29.2 ± 0.7	>99.9	96	42
Cyclohexylacetylene	8.6 ± 0.1	12.5 ± 0.5	28.1 ± 0.5	>99.9	96	0
Phenylacetylene	14.6 ± 0.1	7.2 ± 0.4	26.0 ± 1.0	90	82	0

of the initial substrate and was characterised by the maximum achieved value of this variable in the reaction. The dependence $S_{\max, C=C}$ on the conversion was always identical. At low conversions (<5%), this variable usually reached its maximal value and remained constant up to high conversions (>90%). The values of the maximum acquired concentration of an alkenic substrate in the reaction mixture ($c_{C=C\max}$) also characterised the selective courses of hydrogenation. The stability of individual cycloalkanic substituents was quantitatively characterised by a parameter of concentration of hydrogenolytic products ($c_{H\text{-lysis}}$) after a total replacement of unsaturated substances from the reaction mixture. The stability of cycloalkanic substituents increased in the expected sequence: cyclopropyl < cyclopentyl < cyclohexyl. The extent of hydrogenolytic disintegration of cycloalkanic substituents was significantly higher on palladium catalyst. The cyclohexanic ring did not undergo hydrogenolytic cleavage.

3.2. Hydrogenation of model alkenes

Hydrogenations of ethylenic substrates bearing the same substituents on terminal double bond (cyclopropyl, cyclopentyl, cyclohexyl, phenyl) were also carried out. The reaction scheme corresponded well to the parts of the scheme depicted on Figs. 1 and 2. The values of the initial reaction rates of individual alkenic substrates ($r_{0C=C}$) increased in the following sequence related to both of the catalysts: styrene < cyclohexylethylene < cyclopentylethylene <

cyclopropylethylene (Table 3). This sequence of substrates arranged by an increasing hydrogenation rate of alkenic bond was in opposite order when compared to the sequence of substrates arranged by an increasing hydrogenation rate of alkyne bond. The apparent activation energies, which ranged between 42 and 48 kJ mol⁻¹ on Pt/C and 36–40 kJ mol⁻¹ on Pd/C were evaluated. The Table 3 shows the initial reaction rates of alkenic substrates ($r_{0C=C}$) compared to the values of $r_{C=C}$ (rate of double bond hydrogenation after a total replacement of $C\equiv C$ bond from the reaction mixture). In all cases, a relatively low loss of the catalyst activity was observed ($r_{0C=C}$ versus $r_{C=C}$). The only exception was behaviour of styrene after hydrogenation of phenylacetylene on palladium catalyst. The decrease of the hydrogenation rate of this substrate was almost double compared to the hydrogenation rate of styrene (hydrogenation in the individual arrangement).

3.3. Competitive hydrogenation in binary systems of alkyne substrates

The results of kinetic measurements in binary systems of model alkyne compounds were processed by use of the Rader–Smith Equation [7]. Table 4 presents the resulting values of selectivities of competitive hydrogenations (S_{AB}), relative reactivities (r_{A0}/r_{B0}) and relative adsorptivities (K_A/K_B). The table clearly demonstrates that the values of selectivities of competitive hydrogenations were

Table 3
Results of hydrogenation of substituted ethylenes (individual arrangements)

Substrate	$r_{0C=C}$ (mmol min ⁻¹ g _{cat} ⁻¹)	$r_{C=C}$ (mmol min ⁻¹ g _{cat} ⁻¹)	E_A (kJ mol ⁻¹)
Platinum catalyst			
Cyclopropylethylene	13.2 ± 0.1	12.3 ± 0.5	42.0 ± 1.0
Cyclopentylethylene	10.8 ± 0.1	10.1 ± 0.3	44.5 ± 1.0
Cyclohexylethylene	10.3 ± 0.1	9.5 ± 0.2	45.0 ± 1.0
Styrene	8.8 ± 0.1	8.6 ± 0.2	47.6 ± 1.0
Palladium catalyst			
Cyclopropylethylene	15.0 ± 0.1	14.1 ± 0.5	36.9 ± 1.0
Cyclopentylethylene	13.6 ± 0.1	13.0 ± 0.3	38.2 ± 1.0
Cyclohexylethylene	13.2 ± 0.2	12.5 ± 0.2	37.8 ± 1.0
Styrene	12.8 ± 0.1	7.2 ± 0.2	39.8 ± 1.0

Table 4
Results of competitive hydrogenation in binary systems of substituted acetylenes

Substrate A	Substrate B	S_{AB}	r_{A0}/r_{B0}	K_A/K_B
Platinum catalyst				
Cyclopropylacetylene	Cyclohexylacetylene	1.39 ± 0.02	0.6 ± 0.1	2.4 ± 0.4
Cyclopentylacetylene	Cyclohexylacetylene	1.06 ± 0.03	0.8 ± 0.1	1.4 ± 0.2
Phenylacetylene	Cyclohexylacetylene	4.7 ± 0.1	1.2 ± 0.1	4.0 ± 0.4
Cyclopropylacetylene	Cyclopentylacetylene	1.30 ± 0.03	0.7 ± 0.1	1.9 ± 0.3
Phenylacetylene	Cyclopentylacetylene	4.2 ± 0.1	1.5 ± 0.1	2.8 ± 0.3
Phenylacetylene	Cyclopropylacetylene	3.0 ± 0.1	2.1 ± 0.1	1.4 ± 0.2
Palladium catalyst				
Cyclopropylacetylene	Cyclohexylacetylene	1.26 ± 0.04	0.5 ± 0.1	2.6 ± 0.6
Cyclopentylacetylene	Cyclohexylacetylene	1.02 ± 0.02	0.7 ± 0.1	1.5 ± 0.2
Phenylacetylene	Cyclohexylacetylene	11.1 ± 0.1	1.7 ± 0.1	6.6 ± 0.6
Cyclopropylacetylene	Cyclopentylacetylene	1.11 ± 0.03	0.7 ± 0.1	1.6 ± 0.3
Phenylacetylene	Cyclopentylacetylene	10.9 ± 0.1	2.3 ± 0.1	4.8 ± 0.3
Phenylacetylene	Cyclopropylacetylene	9.8 ± 0.1	3.6 ± 0.1	2.7 ± 0.2

always significantly shifted in favour of phenylacetylene on both of the tested catalysts. The presence of aromatic ring in phenylacetylene molecule caused a higher value of the surface reaction rate as well as a significantly higher value of its adsorptivity compared to cycloalkylacetylenes.

In binary systems of cycloalkylacetylenes, the selectivity of competitive hydrogenation, increased in the sequence: cyclohexylacetylene < cyclopentylacetylene < cyclopropylacetylene. This sequence was opposite to the sequence related to the values of the surface reaction rates of the identical substrates. The differences in the values of reactivities resulting from the effect of a cyclical substituent on C≡C bond were not very significant. Table 4 noticeably infers that during transfer of these model substances to binary systems, a change in their reactivity occurred as a reason of effect of the parameter of adsorptivity, which increased along the above mentioned sequence of selectivities of competitive hydrogenation. The method of competitive hydrogenation does not allow determining absolute values of the adsorption coefficients, but only their relative values. From this reason, the evaluation of stability of the adsorbed complex is, within the sequence of various catalysts, impossible. Therefore, from the values of the relative adsorptivities, it was not possible to express quantitatively a known higher stability of the alkyne-palladium adsorbed complex. Values of relative adsorptivities revealed that there were higher differences in values of this parameter on palladium.

Competitive hydrogenation of acetylenic model substances on both catalysts in reality did not proceed as “pure” competitive hydrogenations in binary systems, but rather included continuously increasing amount of alkenic substances produced as reactive intermediates. For the platinum catalyst, identically as in the competitive hydrogenation in systems where one of the substrates was phenylacetylene on palladium, competitive adsorption and hydrogenation of alkenic intermediates took place. Regardless of this fact, deviations from the linearity of the Rader–Smith equation occurred no earlier than after reaching high conversions

(>90%) of the more reactive alkynic substrate. The only exception were the competitive hydrogenations, in which one of the substrates was phenylacetylene on palladium catalyst, during which deviations from the linearity of the Rader–Smith equation occurred approximately at the point corresponding to 80%-conversion of phenylacetylene. This behaviour was most probably associated with the above-discussed behaviour of phenylacetylene and styrene on palladium catalyst during hydrogenations in individual arrangements. Deviations from the linearity occurred in all binary systems of phenylacetylene (substrate A)—cycloalkylacetylene (substrate B) on Pd/C. Under assumption of a constant value of the surface reaction rates, a decrease of phenylacetylene adsorptivity occurred. Separate experiments proved that the given behaviour is not a result of a decrease of the ratio alkyne/catalyst during the hydrogenation course, but the result of a decrease of the ratio of phenylacetylene/styrene. In the case of arrangement of competitive hydrogenation of cycloalkylacetylene (substrate A)—mixture of phenylacetylene and styrene corresponding to 80%-conversion of phenylacetylene (substrate B), the linearity of the Rader–Smith equation was not fulfilled from the very beginning stages of the competitive hydrogenation.

In binary systems of acetylenic substances, a possibility of an indirect determination of the selectivity of competitive hydrogenation [1] from values acquired for other substrate couples was verified based on assuming validity of the relation:

$$S_{AB} S_{BC} S_{CA} = 1 \quad (1)$$

and:

$$S_{AB} = \frac{1}{S_{BA}} \quad (2)$$

For all possible combinations of the model alkynic substrates, the values of products on the left side of the above Eq. (2) ranged in the interval (0.9–1.1). Based on these results, the possibility of selectivity values estimation from

Table 5
Results of competitive hydrogenation in binary systems of substituted ethylenes

Substrate A	Substrate B	S_{AB}	r_{A0}/r_{B0}	K_A/K_B
Platinum catalyst				
Cyclopropylethylene	Cyclohexylethylene	1.70 ± 0.02	1.3 ± 0.1	1.3 ± 0.1
Cyclopentylethylene	Cyclohexylethylene	1.03 ± 0.02	1.0 ± 0.1	1.0 ± 0.2
Styrene	Cyclohexylethylene	1.80 ± 0.03	0.8 ± 0.1	2.3 ± 0.3
Cyclopropylethylene	Cyclopentylethylene	1.64 ± 0.02	1.2 ± 0.1	1.4 ± 0.1
Styrene	Cyclopentylethylene	1.68 ± 0.02	0.8 ± 0.1	2.1 ± 0.3
Styrene	Cyclopropylethylene	1.10 ± 0.03	0.7 ± 0.1	1.6 ± 0.3
Palladium catalyst				
Cyclopropylethylene	Cyclohexylethylene	2.69 ± 0.04	1.1 ± 0.1	2.5 ± 0.3
Cyclopentylethylene	Cyclohexylethylene	1.28 ± 0.02	1.0 ± 0.1	1.3 ± 0.2
Styrene	Cyclohexylethylene	4.90 ± 0.1	1.0 ± 0.1	4.9 ± 0.6
Cyclopropylethylene	Cyclopentylethylene	2.13 ± 0.03	1.1 ± 0.1	2.0 ± 0.2
Styrene	Cyclopentylethylene	3.80 ± 0.05	0.9 ± 0.1	4.3 ± 0.5
Styrene	Cyclopropylethylene	1.93 ± 0.02	0.8 ± 0.1	2.5 ± 0.3

values acquired independently for alkyne substrates of structurally similar type was confirmed.

3.4. Competitive hydrogenation in binary systems of alkenic substrates

Competitive hydrogenations of ethylenic substrates also allow an evaluation of the effect of the cycloalkyl substituents on the terminal double bond. Analogously as before, selectivities of competitive hydrogenations and values of adsorptivities and reactivities were elucidated from experiments. The data acquired in binary systems very well fulfilled the linearity of the Rader–Smith equation up to high conversions. Numerical values and trends of these parameters are given in the Table 5. The reactivity progression obtained for the binaries (parameter of selectivity of competitive hydrogenation) was analogous to that elucidated at the alkyne systems. In both cases the substituent effect on a molecular behaviour in adsorption is very similar. Styrene adsorptivity was so intense that completely prevailed in the affection of the rate of hydrogenation in the binary system despite the rate of the surface reaction was the lowest for this molecule. In the system of cycloalkanic ethylenes no fluctuation of the surface reaction rates was observed. The parameter of adsorptivity, in this case “self-characterised” as an additive property, increased smoothly in the same direction. It might be concluded that very similar trends of the studied factors, regarding their influence on the adsorption properties of the double bond were encountered (as before for the triple bond).

A possibility of an indirect determination of the selectivity of competitive hydrogenation from values acquired for other substrate couples was also verified in the binary systems of ethylenic substances (relations (2) and (3)). For all possible combinations in binary systems, the values of products on the left side of the Eq. (2) ranged in the interval (0.9–1.1).

4. Conclusion

In a series of cycloalkyl substituted acetylenes and ethylenes, the problem of the structural effect of a reacting substance—cyclic substituent on a terminal unsaturated carbon–carbon bond—on hydrogenation course on platinum and palladium supported catalysts was studied. The kinetic method studying structural effects allowed expressing the effects of molecular structural fragments on the surface reaction rate and the stability of an adsorbed complex.

Acknowledgements

The authors hereby acknowledge their gratitude to the Grant Agency of the Czech Republic (Grant 104/00/1009) and the Ministry of Education of the Czech Republic (Grant Cez:Msm 223 100001) for their financial support granted to this project.

References

- [1] L. Červený, V. Růžička, Adv. Catal. 30 (1981) 335.
- [2] L. Červený, V. Růžička, Catal. Rev. Sci. Eng. 24 (1982) 503.
- [3] P. Kačer, L. Červený, Appl. Catal. 229 (2002) 193.
- [4] M. Kraus, G. Ertl (Ed.), H. Knözinger (Ed.), J. Weitkamp (Ed.), Handbook of Heterogeneous Catalysis, VCH Verlagsgesellschaft mbH, Weinheim, 1997, p. 1051.
- [5] D.S. Jackson, L.A. Shaw, Appl. Catal. 134 (1996) 91.
- [6] D.S. Jackson, G.J. Kelly, Curr. Top. Catal. 1 (1997) 47.
- [7] C.P. Rader, H.A. Smith, J. Am. Chem. Soc. 84 (1962) 1443.
- [8] A. Sarkany, J. Catal. 180 (1998) 149.
- [9] E. Lamy-Pitaro, B. N'Zemba, J. Barbier, F. Barbot, L. Miginiac, J. Mol. Catal. 142 (1999) 39.
- [10] P. Kačer, J. Tobičák, L. Červený, J. Mol. Catal. 195 (2003) 235.
- [11] G. Carturan, G. Facchin, G. Cocco, S. Enzo, G. Navazio, J. Catal. 76 (1982) 405.