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Molecular structure effects in hydrogenation of allyl and vinylethers on platinum and palladium supported catalysts

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Abstract

The work is concerned with structure effects exerted by molecules of alkylvinylethers and allylalkylethers in heterogeneously catalysed hydrogenation on platinum and palladium catalysts. The method of a competitive hydrogenation is suggested as a suitable kinetic tool for discussion of stability of surface complexes and of a rate of surface reactions in terms of structures of reacting molecules. Experimental data, represented here by parameters of adsorptivity and reactivity, are interpreted with the help of molecular modelling.
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1. Introduction

Molecular structure effects of alkenic reactants in heterogeneously catalysed hydrogenations have thoroughly been investigated in the past [1–4]. Mostly experimental observations were accomplished with a range of quantitative relationships derived on a basis of the linear free energy (LFER) principle. With the progress of molecular modelling and availability of modern analytical methods, the general validity of empirical correlations should be critically reassessed. Molecular simulation allows a complex treatment of experimental data on an atomic and molecular scale. Potentially it also involves a theoretical interpretation of a catalytic surface properties and conditions of the catalyst–molecule activated complex existence. Generally vague terms such as selectivity of a catalytic reaction [5], reactant surface adsorptivity, competitive reactivity, etc., might be effectively redefined.

In this work, molecular structure effects are discussed with the intention of the quantitative description of the below listed phenomena [1,2,6,7] for a series of congenial alkenic ethers (allylalkylethers and vinylethers):

- effect of a molecular bulkiness (steric constrains of an alkyl part);
- effect of a mutual location of a C=C bond and an atom of oxygen (propylvinylether versus allylpropylether);
- effect of the presence/absence of the etheric oxygen atom (allylbenzene versus allylphenylether);
- effect of the presence/absence of the alkyl part located on a CH_2=CH–CH_2–O– structural skeleton (allylalcohol versus allylphenylether; allylalcohol versus allylpropylether).

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The method of the competitive hydrogenation represents a useful tool for the in situ evaluation of surface processes. It allows a discussion of rate effects of molecular fragments and of the stability of adsorbed surface complexes [1,2,8–12]. It involves typically two substrates reacting in parallel and thus competing for adsorption on available surface active sites. It is supposed that a magnitude of adsorptivity of a substrate, which is a key factor in its catalytic transformation, invariably depends on the properties and energies of frontier orbitals directly interacting [5,13,14] with catalytic active sites (the catalyst is treated here as a constant property).

2. Experimental

2.1. Chemicals

All reactants were freshly distilled before use. Propylvinylether, *iso*-butylvinylether, *sec*-butylvinylether, *tert*-butylvinylether, allylethylether, allylpropylether, allylphenylether, allylalcohol and allylbenzene were supplied by Aldrich, USA. Reactions were carried out in a solvent—methanol p.a. (Penta, Czech Republic) and with hydrogen 4.0 (Linde, Czech Republic).

2.2. Catalysts

The elemental crystallite size (XRD 3000, CoKα source of radiation, Rich. Seifert & Co., Germany), the total surface area (BET N_2/77 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); and 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 of CO/Pd equal to 1/2.

Table 1
Characteristics of the used catalysts

Catalyst (%)	Grain size (mm)	Particle size (nm)	S_{BET} (m^2/g_{CAT})	S_{metal} (m^2_M/g_{CAT})
3 Pd/C	<0.02	20.2	1161	32.8
5 Pt/C	<0.05	15.5	778	45.3

2.3. Apparatus and a typical experiment

Kinetic measurements were carried out isothermally at 298 K in a stirred batch reactor in methanol in a kinetic regime. Consumption of hydrogen was continuously recorded [15] and samples of a reaction mixture were withdrawn at chosen time intervals for a GC analysis (HP 5890, H & P, USA, fitted with a capillary column HP 20M—50 m × 0.32 mm × 0.32 μm). Typically, 2 mmol of a reactant (1 mmol + 1 mmol for competitive binary reactions) were introduced in the reactor in 15 ml of methanol (amount of a catalyst 0.01–0.001 g).

2.4. Molecular modelling

Semi-empirical PM3 method [16] available in HyperChem (Hypercube, USA) was used for searching (grid-search) of potential energy surfaces (global minima) of studied molecules.

3. Results and discussion

3.1. Hydrogenation of model molecules

Members of the three independent series of model molecules (alkylvinylethers—propylvinylether, *iso*-butylvinylether, *sec*-butylvinylether, *tert*-butylvinylether; allylalkylethers—allylethylether, allylpropylether, allylphenylether; referential molecules—allylalcohol, allylbenzene) were individually hydrogenated over platinum and palladium catalysts. Initial reaction rates were evaluated from experimental data (collected in a form of concentration versus time plots) and used in calculations of relative adsorption coefficients.

Generally total conversions of alkylvinylethers were attained on both the types of catalysts. The reactions were treated as simple one step transformations A → B of the zero order to the reacting molecules up to very high conversions. Similar trends were also observed for hydrogenations of allylalkylethers, allylbenzene and allylalcohol on the platinum catalyst (Fig. 1). On the other hand, the transformation of allylic molecules on the palladium catalyst was accompanied by a

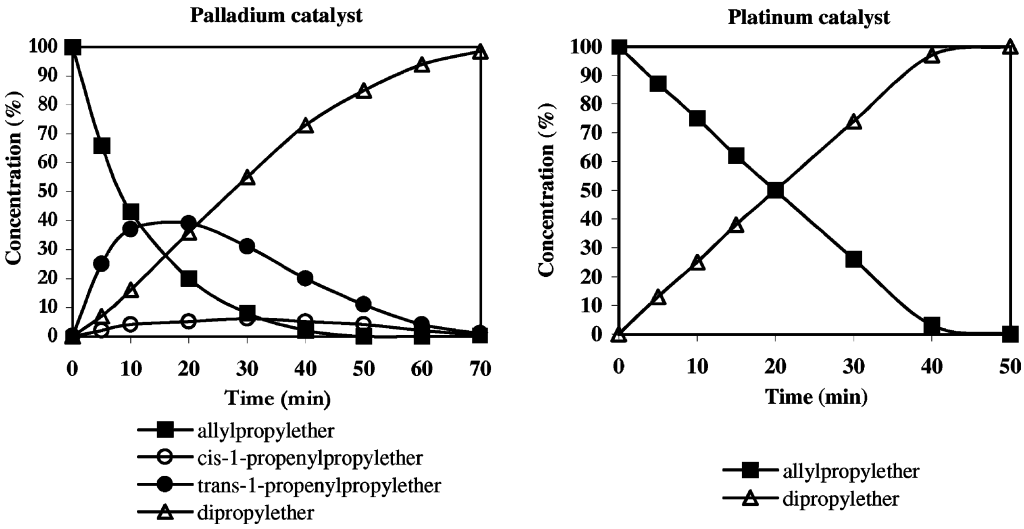

Fig. 1. The course of hydrogenation of allylpropylether on palladium and platinum catalysts.

parallel shift of a double bond to the thermodynamically more favourable position 2 with (*E*) and (*Z*) geometric isomers. Typically for allylalcohol, this isomerisation also yielded a more stable molecule of propanal (transition from the enol- to the oxo-form). Initial reaction rates of hydrogenation of allylic compounds were evaluated as the first derivative of the functionality of concentration on time in point $t = 0$ min. Values of initial reaction rates are listed as shown in Table 2.

3.2. The method of competitive hydrogenation

The method of the competitive hydrogenation represents an important tool for the in situ evaluation of the surface adsorption and allows a discussion of rate effects of molecular structural fragments and stability of adsorbed surface complexes. If kinetics of reactions involved is describable by identical equations, then the factor S_{AB}, usually referred to as the selectivity of the competitive hydrogenation, could be evaluated by means of the Rader–Smith equation [17]:

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

Ideally the dependence of $\log(c_A/c_{A0})$ on $\log(c_B/c_{B0})$ is graphically expressed as a straight line with a gradient providing S_{AB}. When this value is obtained, evaluation of the relative adsorption coefficients, K_A/K_B [1,2] is straightforward. Initial reaction rates of hydrogenations of individual substrates r_0 are usually used as inputs to (1) instead of rate constants k_{AH} and k_{BH}. Values of S_{AB}, and r_{A0}/r_{B0}, obtained from experiments with individual substrates and from competitive hydrogenations in binary systems constitute a basis for

Table 2
Initial reaction rates for model molecules

Catalyst	Substrate	r_0 (mmol min^{-1} g$_{CAT}^{-1}$)
Pd/C	Propylvinylether	18.7 ± 0.4
	iso-Butylvinylether	17.1 ± 0.3
	sec-Butylvinylether	15.9 ± 0.3
	tert-Butylvinylether	2.8 ± 0.1
	Allylethylether	56.6 ± 0.5
	Allylpropylether	50.6 ± 0.5
	Allylphenylether	62.3 ± 0.5
	Allylalcohol	73.0 ± 1.0
	Allylbenzene	26.0 ± 1.0
Pt/C	Propylvinylether	13.5 ± 0.2
	iso-Butylvinylether	11.4 ± 0.2
	sec-Butylvinylether	10.9 ± 0.2
	tert-Butylvinylether	1.9 ± 0.1
	Allylethylether	6.8 ± 0.1
	Allylpropylether	6.5 ± 0.1
	Allylphenylether	7.9 ± 0.1
	Allylalcohol	7.5 ± 0.1
	Allylbenzene	9.8 ± 0.2

the discussion of structure effects on reactivity and adsorptivity of model molecules.

3.3. Molecular modelling

The reactions were theoretically evaluated assuming the catalytic surface as an invariable (constant) property, not undergoing any changes and not exerting any specific effects. Model variables, exclusively on the side of the molecule, were assessed by the semi-empirical method. A magnitude of adsorptivity of a substrate, a key factor in the catalytic transformation of a molecule, invariably depends on properties and energies of frontier orbitals directly interacting with the catalyst. The premise that trends in structure effects of reacting molecules (in series of the structure similar substrates) could be interpreted by means of properties of the frontier orbitals was accepted. Theoretical concepts of changes in efficiency of the frontier orbitals superposition in adsorption of substrates and speculations on changes in the two-electrons interaction and the four-electrons repulsion were examined. The shift of the frontier orbitals of a molecule eventuates either intensification or weakening of mutual interactions of the adsorbent (surface) and the adsorbate (molecule). The trend in energies of frontier orbitals among structure congenial molecules is associable with changes observed in the catalytic hydrogenations. A translation of the $\pi_{c=c}$ energetic level toward a higher energy results in its relative shift regarding the Fermi's level of the catalytic metal. This phenomenon operates in parallel with a decrement of the four-electrons repulsion with the d-orbitals of a metal and thus stabilising the forming surface complex. Conversely, a shift of the $\pi^*_{c=c}$ toward a higher energy level pursuits a depression of two-electron interactions to occupied levels on the catalytic surface and destabilises the complex. These principles are "behind" the theoretical consideration of the stability of forming surface complexes.

3.4. Effect of the substituent "bulkiness"

Quantification of structure ruling effects of the spatial size of the alkyl substituent in series of alkylvinylethers (propylvinylether, *iso*-butylvinylether, *sec*-butylvinylether, *tert*-butylvinylether) on kinetics of the surface reaction (Pt, and Pd catalysts) and on the stability of the activated surface complex was experimentally endeavoured. Kinetic results represented here by selectivities of competitive hydrogenations, relative reactivities and relative adsorptivities are given in Table 3. The data reveal the structure of the alkyl substituent affects substantially reactivities in binary systems and rates of surface reactions of individual substrates (propylvinylether > *iso*-butylvinylether $\sim$ *sec*-butylvinylether $\gg$ *tert*-butylvinylether). An affection of adsorptivity values was generally proved insignificant with exception of (not well pronounced) lowering of adsorptivity observed for the *tert*-butyl

Table 3
Kinetic data of competitive hydrogenations in binary systems of alkylvinylethers

Substrate A	Substrate B	S_{AB}	r_{A0}/r_{B0}	K_A/K_B
Palladium catalyst				
Propylvinylether	*tert*-Butylvinylether	16.4 ± 0.4	6.7 ± 0.4	2.5 ± 0.2
iso-Butylvinylether	*tert*-Butylvinylether	12.8 ± 0.2	6.1 ± 0.3	2.1 ± 0.1
sec-Butylvinylether	*tert*-Butylvinylether	12.0 ± 0.2	5.7 ± 0.3	2.1 ± 0.2
Propylvinylether	*sec*-Butylvinylether	1.38 ± 0.02	1.2 ± 0.1	1.2 ± 0.1
iso-Butylvinylether	*sec*-Butylvinylether	1.08 ± 0.03	1.1 ± 0.1	1.0 ± 0.1
Propylvinylether	*iso*-Butylvinylether	1.22 ± 0.02	1.1 ± 0.1	1.1 ± 0.1
Platinum catalyst				
Propylvinylether	*tert*-Butylvinylether	12.5 ± 0.2	7.1 ± 0.5	1.7 ± 0.2
iso-Butylvinylether	*tert*-Butylvinylether	10.8 ± 0.1	6.0 ± 0.4	1.8 ± 0.2
sec-Butylvinylether	*tert*-Butylvinylether	10.7 ± 0.2	5.8 ± 0.4	1.8 ± 0.2
Propylvinylether	*sec*-Butylvinylether	1.22 ± 0.03	1.2 ± 0.1	1.0 ± 0.1
iso-Butylvinylether	*sec*-Butylvinylether	1.01 ± 0.02	1.0 ± 0.1	1.0 ± 0.1
Propylvinylether	*iso*-Butylvinylether	1.17 ± 0.02	1.2 ± 0.1	1.0 ± 0.1

Table 4
Energies of frontier orbitals of alkylvinylethers

Alkyl group	E_{HOMO} (eV)	E_{LUMO} (eV)
Methyl	−9.620	1.250
Ethyl	−9.593	1.271
Propyl	−9.596	1.257
Butyl	−9.598	1.257
iso-Propyl	−9.535	1.285
iso-Butyl	−9.580	1.255
sec-Butyl	−9.530	1.282
tert-Butyl	−9.473	1.343

substituent. Conspicuously much wider gap (an order of magnitude) between reactivities of the *tert*-butyl substituted molecule and other members of the series was responsible for its (*tert*-butyl) different behaviour upon hydrogenation.

Molecular modelling results (Table 4) did not reveal any important influence of linear alkyl substituents on positions of frontier orbitals. Differences in a series of not branched alkyls were marginal and the observed variations in adsorptivities of individual reactants likely corresponded to geometric effects of a substituent and to the participation of the four-electrons repulsion between the substituent and the active centre. In the series of branched alkylvinylethers (*iso*-butyl < *sec*-butyl < *tert*-butyl) energies of HOMO and LUMO orbitals increased in the same direction. Certain decrease of the four-electrons repulsion between the $\pi_{c=c}$ adsorbate orbital and d-orbitals of the adsorbent (in this series) was expected. In parallel, the increasing tendencies of the two-electrons interaction with anti-bonding orbitals of a metal were detected. This entirely positive effect of the adsorbed surface complex stabilisation is accompanied by the less favoured "back-bonding" process. Its direct implication is completely opposite—the complex destabilisation due to the increasing energy of the $\pi^*_{c=c}$ orbital.

Little substituent effect on the double bond orbitals accounts for its isolation in the molecule by means of the atom of oxygen. These specific attributes given by the presence of electronic effects decrease rapidly with an increasing distance from the bond. The same also applies for the interpretation of only a limited effect of alkyls on the double bond in vinylethers. Energetically the most stable conformations of adsorbate molecules (R–O–CH=CH_2) obtained by the grid search method possess the alkyl function oriented above the plane of the double bond. Practically it means that neither a significant interaction between the active site and the function (alkyl), nor any steric affection of the adsorptivity by linear alkyls are expected.

It is obvious (Table 4) the branched alkyls behave differently. Interactions of *sec*-butylvinylether and *iso*-butylvinylether with a catalytic surface may theoretically also cover conformations when alkyls are not involved. On the other hand, for *tert*-butylvinylether the interaction of the substituent (alkyl) with surface sites must not be omitted (Fig. 2).

Substituent effects experimental data in a series—allylethylether, allylpropylether, allylphenylether are comprised as shown in Table 5. Identical adsorption and kinetic properties were found for the linear alkyls (ethyl, and propyl). Allylphenylether exhibited a very similar magnitude of the rate of the surface reaction as other model substrates due to the strong adsorptivity effect caused by the presence of the aromatic ring in its molecule.

Molecular modelling (Table 6), as previously mentioned (alkylvinylethers), yielded only insignificant

Table 5
Kinetic data of competitive hydrogenations in binary systems of allylalkylethers

Substrate A	Substrate B	S_{AB}	r_{A0}/r_{B0}	K_A/K_B
Palladium catalyst				
Allylphenylether	Allylethylether	3.30 ± 0.04	1.1 ± 0.1	3.0 ± 0.3
Allylphenylether	Allylpropylether	3.36 ± 0.02	1.2 ± 0.1	2.8 ± 0.3
Allylpropylether	Allylethylether	1.01 ± 0.03	0.9 ± 0.1	1.1 ± 0.2
Platinum catalyst				
Allylphenylether	Allylethylether	2.48 ± 0.04	1.2 ± 0.1	2.1 ± 0.2
Allylphenylether	Allylpropylether	2.23 ± 0.04	1.2 ± 0.1	1.9 ± 0.2
Allylpropylether	Allylethylether	0.98 ± 0.03	1.0 ± 0.1	1.0 ± 0.1

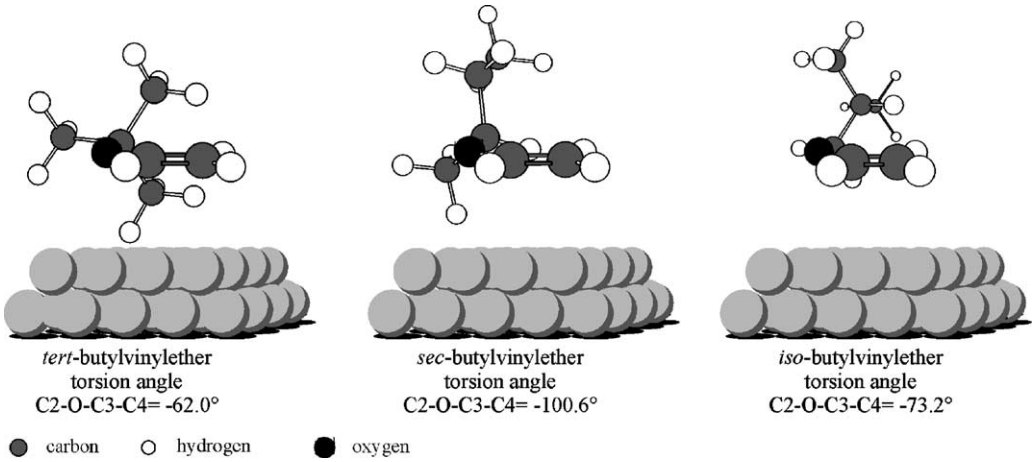

Fig. 2. Calculated conformations of alkylvinylethers that could be theoretically detected on the catalytic surface.

differences in magnitudes of frontier orbitals for allylalkylethers due to the location (distance) of the structural moiety from the double bond. Allylphenylether with highest occupied energetic levels of frontier orbitals was the only exception. Much higher adsorptivity due to the stabilisation of the forming surface complex (interaction of the aromatic ring with the active particle) was probably the reason. The alkyl part directed above the plane of the double bond was identified as the most stable conformation with the implication of minimisation of repulsion between the alkyl chain and the catalytic surface.

In the systems reported, the method of the indirect evaluation of the selectivity of the competitive hydrogenation [1,2] was also tested. The method is based on the idea of using selectivity values determined from two binaries having one common member for the estimation of the selectivity of a third mixture (combined) that has not been experimentally studied. A simple equation functions as a relation of these three values:

$$S_{AB} \cdot S_{BC} \cdot S_{CA} = 1 \quad (2)$$

and by definition

$$S_{AB} = \frac{1}{S_{BA}}. \quad (3)$$

Despite some limitations theoretical implications of this approach might be useful in assessment of the extent of specific interactions of various nature and origin in competitive hydrogenations. As long as a product (Eq. (2)) of independently obtained values approaches 1, specific interactions targeting just one of the reactants are, with a good confidence, absent. If the deflection from 1 rises, the system is more affected by specific interactions and discussed structural effects are not the only variables (Table 7).

Table 6
Energies of frontier orbitals of allyalkylethers

Alkyl group	E_{HOMO} (eV)	E_{LUMO} (eV)
Methyl	10.319	0.956
Ethyl	10.292	0.972
Propyl	10.295	0.967
Butyl	10.296	0.967
Phenyl	9.162	0.329

3.5. *Effect of the mutual location of the C=C bond and the atom of oxygen in molecules of unsaturated ethers*

Attention has also been paid to the role of the oxygen atom with respect to the C=C location in molecules of propylvinylether and allylpropylether (systems with Pt and Pd catalyst). The finding (Table 8) that the course of the reaction was subjected to the type of a catalyst used was, beyond controversy, the most striking result of this group of experiments. Systems with platinum catalysts behaved as expected.

Table 7
Indirect evaluation of the selectivity of the competitive hydrogenation

Substrate	S_{AB}	S_{BC}	S_{CA}	$S_{AB} \cdot S_{BC} \cdot S_{CA}$
Palladium catalyst				
(A) Propylvinylether (B) *iso*-Butylvinylether (C) *sec*-Butylvinylether	1.22	1.08	1/1.38	0.96
(A) Propylvinylether (B) *iso*-Butylvinylether (C) *tert*-Butylvinylether	1.22	12.8	1/16.4	0.95
(A) Propylvinylether (B) *sec*-Butylvinylether (C) *tert*-Butylvinylether	1.38	12.0	1/16.4	1.01
(A) *iso*-Butylvinylether (B) *sec*-Butylvinylether (C) *tert*-Butylvinylether	1.08	12.0	1/12.8	1.01
(A) Allylethylether (B) Allylpropylether (C) Allylphenylether	1/1.01	1/3.36	3.30	0.97
Platinum catalyst				
(A) Propylvinylether (B) *iso*-Butylvinylether (C) *sec*-Butylvinylether	1.17	1.01	1/1.22	0.97
(A) Propylvinylether (B) *iso*-Butylvinylether (C) *tert*-Butylvinylether	1.17	10.8	1/12.5	1.01
(A) Propylvinylether (B) *sec*-Butylvinylether (C) *tert*-Butylvinylether	1.22	10.7	1/12.5	1.02
(A) *iso*-Butylvinylether (B) *sec*-Butylvinylether (C) *tert*-Butylvinylether	1.01	10.7	1/10.8	1.00
(A) Allylethylether (B) Allylpropylether (C) Allylphenylether	1/0.98	1/2.23	2.48	1.13

Table 8
Kinetic data of competitive hydrogenations in the system allylpropylether: propylvinylether

Substrate A	Substrate B	S_{AB}	r_{A0}/r_{B0}	K_A/K_B
Palladium catalyst				
Allylpropylether	Propylvinylether	4.9 ± 0.1	2.7 ± 0.1	1.8 ± 0.1
Platinum catalyst				
Allylpropylether	Propylvinylether	0.20 ± 0.02	0.5 ± 0.1	0.4 ± 0.1

Table 9
Energies of frontier orbitals of alkyl-1-propenylethers

Alkyl group	E_{HOMO} (eV)	E_{LUMO} (eV)
Alkyl-(*E*)-1-propenylether		
Methyl-	−9.245	1.188
Ethyl-	−9.219	1.206
Propyl-	−9.226	1.193
Butyl-	−9.227	1.194
Alkyl-(*Z*)-1-propenylether		
Methyl-	−9.208	1.173
Ethyl-	−9.165	1.220
Propyl-	−9.171	1.209
Butyl-	−9.171	1.209

The reactivity in a binary mixture (that is, the selectivity of the competitive hydrogenation) was shifted in favour of vinylether as justified by values of relative reactivities and adsorptivities (Table 8). On the other hand, in systems with the palladium catalyst allylethers were preferred. Isomerisation properties of palladium are well known and likely take part here as well. Utilisation of the palladium catalyst allowed migration of a double bond in a molecule in the direction of the energetically (thermodynamically) more favourable state. The isomer with the C=C located in the position 2 with the prevailing *trans* arrangement was the most stable one under studied conditions. It is believed that the observed differences, in identical competitive transformations, catalysed by either platinum or palladium are due to the described special properties of the second metal. In fact the competitive hydrogenation of 1-propenylpropylether with the corresponding vinylether rather took part than the originally expected allylpropylether with propylvinylether.

The hypothesis validity was theoretically tested by modelling *cis*- and *trans*-isomers of 1-propenylalkylethers. Significant differences in energies of frontier orbitals of allylalkylethers and 1-propenylalkylethers were found (Tables 6 and 9). Energetic levels of the $\pi_{c=c}$ and $\pi^*_{c=c}$ orbitals of the latter were shifted toward higher values, hence variations in adsorptivities of allylethers and their position isomers were expected. The two-electron interactions between the HOMO orbital of the adsorbate and vacant orbitals of the active site were evaluated for 1-propenylalkylethers. This phenomenon operates in parallel with a shift of the energetic level of LUMO orbitals with a direct consequence in the decline of the back-bonding and weakening of the forming surface complex. Energy of LUMO orbitals was, however, affected much less than that of HOMO orbitals and thus the back-bonding depression was also less significant. The positive effect of the shift in energies of HOMO orbitals on adsorptivity prevailed and 1-propenylalkylether—the metal complex was more stable than the complex allylether—the metal. From comparison of locations of frontier orbitals of 1-propenylalkylethers and of corresponding vinylethers was concluded that HOMO orbitals of the latter group were located on lower levels. LUMO orbitals energies displayed the opposite trend. This antipodal behaviour points on lower adsorptivity of vinylethers in comparison with 1-propenylalkylethers. In the particular case of a system with the palladium catalyst, experimental and theoretical data coincide perfectly, if the isomerisation process detailed previously is taken into account again. It means that a higher adsorptivity of allylether was found on palladium in the system of allylpropylether–propylvinylether.

3.6. Effect of the absence or presence of the etheric oxygen atom and of the alkyl group

Effect of the presence of the oxygen atom was assessed (Table 10) in the binary system allyphenylether : allylbenzene (Pt, Pd). Corresponding reactivities (expressed through the parameter of the competitive hydrogenation selectivity) were shifted in favour of allylphenylether on both the catalysts (much higher adsorptivity of this molecule). Another explanation might be sought in terms of the participation of

Table 10
Kinetic data of competitive hydrogenations in the system allylphenylether : allylbenzene

Substrate A	Substrate B	S_{AB}	r_{A0}/r_{B0}	K_A/K_B
Palladium catalyst				
Allylphenylether	Allylbenzene	7.1 ± 0.1	2.4 ± 0.1	3.0 ± 0.2
Platinum catalyst				
Allylphenylether	Allylbenzene	1.98 ± 0.04	0.8 ± 0.1	2.5 ± 0.4

Table 11
Kinetic data of competitive hydrogenations in the system allylalkylether : allylalcohol

Substrate A	Substrate B	S_{AB}	r_{A0}/r_{B0}	K_A/K_B
Palladium catalyst				
Allylpropylether	Allylalcohol	0.77 ± 0.02	0.7 ± 0.1	1.1 ± 0.2
Allylphenylether	Allylalcohol	1.76 ± 0.04	0.9 ± 0.1	2.0 ± 0.3
Platinum catalyst				
Allylpropylether	Allylalcohol	0.89 ± 0.06	0.9 ± 0.1	1.0 ± 0.2
Allylphenylether	Allylalcohol	1.67 ± 0.02	1.1 ± 0.1	1.5 ± 0.2

the stabilising non-bonding electron pairs located on the atom of oxygen and formed on the adsorbed complex. Surface reaction rate was higher for allylbenzene on Pt, while on Pd a synergistic effect of this parameter with the parameter of adsorptivity was observed promoting the allylphenylether transformation.

A similar effect of the alkyl group located on the structural unit CH_2=CH–CH_2–O– was studied in a binary system allylalkylether : allylalcohol (Table 11). The presence of a linear alkyl shifted (allylpropylether) the parameter of selectivity toward allylalcohol (Pd, Pt) likely due to the higher surface rate of this molecule transformation. Stabilities of adsorbed complexes of both members of the pair were comparable. They coincide well with the finding that the non-branched alkyls (due to their conformation and negligible electronic impact on C=C) affect adsorption properties of alkenic ethers only very little. On the other hand, when aromatic allylphenylether was involved the selectivity parameter indicated a preferential transformation of this molecule, obviously due to a higher stability of its surface complex (at nearly identical rates of surface reactions for both transforming types of molecules).

4. Conclusion

Variation in a molecular structure in a series of alkenic ethers (alkylvinylethers and allylalkylethers) has direct implications in a stability of surface complexes and in magnitudes of reaction rates upon hydrogenations on palladium and platinum catalysts. This kinetic method accomplished a discussion of molecular structure effects in this kind of transformation. Experimentally observed trends in adsorptivities and reactivities were interpreted by means of molecular modelling. It was proposed and then successfully tested that the selectivity trends might be interpreted in terms of the properties of corresponding frontier orbitals.

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