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Short Communication

New phenomenon in competitive hydrogenation of binary mixtures of activated ketones over unmodified and cinchonidine-modified Pt/alumina catalyst

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ABSTRACT

Competitive hydrogenations of eight binary mixtures of ethyl pyruvate (EP), methyl benzoylformate (MBF), ketopantolactone (KPL), pyruvic aldehyde dimethyl acetal (PA) and trifluoroacetophenone (TFAP) on platinum/alumina catalysts unmodified (racemic hydrogenation) and modified by cinchonidine (chiral hydrogenation) were studied under the experimental conditions of the Orito reaction. Reaction rates of chiral and racemic hydrogenations were determined and relative adsorption coefficients were calculated. In the competitive chiral hydrogenation of EP + MBF, EP + TFAP and KPL + MBF binary mixtures a new phenomenon was observed: namely the EP and KPL are hydrogenated faster than MBF and TFAP, whereas in racemic one the MBF and TFAP are hydrogenated faster than EP or KPL. Effects of the activated ketones structure on their reactivity and the stability of the surface complexes are discussed. It was found that differences in rate enhancement are caused by the differences both in the adsorptivity and in the reactivity of adsorbed substrates and adsorbed intermediate complexes.

1. Introduction

Competitive hydrogenation of mixtures of ketones over metal catalysts is a widely used method in studies on the mechanism of different types of organic compounds [1–8]. Results obtained have been reviewed on a continuous basis [9–13]. Studies on competitive hydrogenations have yielded new information on the effect of the electronic and 3-D structure of the hydrogenated substrates on their adsorption and on the surface reactions. Concerning the Orito reaction (Scheme 1), to our best knowledge, no results have been published on the competitive hydrogenation of substrate binary mixtures other than our preliminary report [14]. Experimental data of this type is expected to yield new information on this otherwise widely studied enantioselective catalytic hydrogenation. The objective of recent studies on heterogeneous enantioselective hydrogenation of activated ketones over cinchona modified Pt catalysts has mainly been focused on a better understanding of the reaction mechanism, *i.e.* to interpret the origin of enantiodifferentiation and rate enhancement (RE) on this context (summarized in [15–20]).

The aim of the present research was to study the hydrogenation in a batch reactor of eight binary mixtures selected from the activated ketones shown in Fig. 1, with special emphasis on the comparison of reactions using unmodified (racemic hydrogenation) and cinchonidine(CD)-modified catalysts (enantioselective or chiral hydrogenation). Published experimental data of the individual model compounds shown in Fig. 1 are summarized in Table 1[21–28]. The present study on the hydrogenation of these binary mixtures led to unexpected experimental observations.

2. Experimental

2.1. Materials

CD (Fluka), substrates (EP, MBF, PA, TFAP, KPL), toluene and acetic acid were purchased from Aldrich. EP, MBF, PA and TFAP were further purified by vacuum distillation using a Vigreaux-column. KPL was subjected to azeotropic distillation with toluene to remove water. The catalyst, Engelhard 5% Pt/Al_2O_3 (E4759) was pretreated in a fixed-bed reactor in H_2 flow at 673 K as previously described [21].

2.2. Hydrogenations

Hydrogenations were performed in an atmospheric batch glass reactor of 10 mL volume as previously reported [21]. Standard conditions were: 25 mg E4759 catalyst, 5 mL solvent, 1 mmol substrate whereas in case of binary mixtures 1 + 1 mmol of the two substrates, modifier concentration 0.8 mM, 1 bar H_2 pressure, room temperature, 900–1200 rpm (no diffusion control [26,32]). Product analysis has been described previously [29–32]. Hydrogenation rates were calculated in mmol substrate × mg catalyst^{-1} × min^{-1}.

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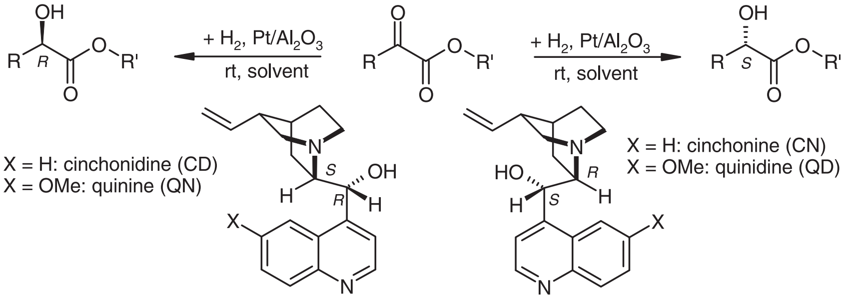

Scheme 1. The Orito reaction.

3. Results and discussions

Only few experimental observations have been reported on the racemic and enantioselective hydrogenation of individual activated ketones under otherwise identical experimental conditions (Table 1). Studies on the competitive hydrogenation of binary mixtures under completely identical conditions have only been described in one preliminary report [14]. One conclusion, already generally accepted (see for example in the reviews published in the last four years [15–19]) is that chiral hydrogenations usually proceed at higher rates (RE: rate enhancement) than do racemic hydrogenations. In the case of ethyl benzoylformate (EBF), however, the difference is smaller, and the ratio of rates may even be inverted depending on the experimental conditions [20,23,24].

The results of the measurements using the EP + PA and KPL + MBF binary mixtures are presented in Figs. 2 and 3, the data obtained using other mixtures are attached in the Supporting Material. Each figure contains 8 measurement series, which are the following: 4 data series on unmodified (racemic hydrogenation: 1_{Ri}, 1_{Rm}, 2_{Ri}, 2_{Rm}; where subscript i: individual and m: mixture) and 4 data series on modified catalyst (chiral hydrogenation: 1_{Ci}, 1_{Cm}, 2_{Ci}, 2_{Cm}). As regards the reaction conditions, the experiments were performed in the two solvents that had been found the most effective in the chiral hydrogenation of the activated ketone EP, *i.e.* in toluene (A) and in acetic acid (B) [15,20,33]. Attempts in the literature to generalize the results in the field of heterogeneous catalysis in terms of solvent properties have not been successful. This statement is especially valid for chiral hydrogenations [20], since there are a number of factors that may play an essential role in determining the rate and selectivity and consequently the mechanism of the hydrogenations [10,20,33–37]. Such factors are the interaction of the solvents with the catalyst, the substrate and the modifier, solubilities of the liquid and gaseous reactants, the competitive adsorption of the solvents, catalyst deactivation caused by the solvent, and possible effect of the solvent on the conformation of the chiral modifier, to mention just the most important ones.

Comparison, under identical experimental conditions, of the hydrogenation rates of individual substrates with that obtained in binary mixtures allows the recognition of certain relationships, some of which have proved to be not only unexpected but also surprising in view of the presently available knowledge. Results calculated from the measured data are summarized in Tables 2 and 3.

3.1. Hydrogenation of individual substrates

As shown in Table 2 entries 1–5, the hydrogenation rates of the individual activated ketones can be arranged in the following order. r_{Ci} and r_{Ri} in toluene are: KPL > MBF ~ EP > PA ~ TFAP; r_{Ci} in AcOH: KPL > MBF > EP ~ PA > TFAP; and r_{Ri} in AcOH: KPL > MBF > EP > TFAP > PA. In other words, in all cases studied KPL is hydrogenated prominently faster than any of the other substrates, whereas PA and TFAP are hydrogenated at the slowest rate. This tendency may be correlated with their adsorbabilities.

Regarding the r_{Ci}/r_{Ri} ratio measured under the identical experimental conditions specified in the Experimental section, the following conclusions can be drawn: (i) $r_{Ci}/r_{Ri} > 1$ for all substrates and (ii) the value of r_{Ci}/r_{Ri} is the largest in hydrogenations of TFAP, KPL and PA in toluene and in hydrogenations of PA and KPL in AcOH. These results for individual substrates serve for useful comparison with those obtained in competitive hydrogenations of binary mixtures (see below).

3.2. Competitive hydrogenations in binary systems

The results calculated from the kinetic data presented in Figs. 2 and 3 and in the Supporting Material corroborate certain prognosticated experimental results [29,38,39], namely that depending on substrates the rates of competitive hydrogenations exhibit significant differences relative to hydrogenations of the individual compounds (see Table 2).

In the chiral hydrogenations of the substrate mixtures in toluene (AcOH) the reaction rates (r_{Cm}) vary depending on the other substrate within the following intervals: EP 0.51–1.72 (0.24–0.70), MBF 0.24–1.24 (0.24–1.12), KPL 3.28–3.92 (2.3–7.4), PA 0.04–0.16 (0.04–0.15), and TFAP 0.17–0.20 (0.03–0.05). Chiral hydrogenations in toluene are generally faster than those in AcOH. r_i is generally larger than r_m (in some cases $r_i \approx r_m$). Comparison of the data summarized in Table 2 also raises other intriguing questions. However, the most unexpected results of these experiments are: (i) it should be emphasized that strikingly high r_C/r_R ratios were observed in the hydrogenation of certain binary mixtures mainly in acetic acid (Table 2: entries 6, 9, 14, 16, 19) as compared to the ratios for hydrogenations of individual substrates; (ii) in the competitive chiral hydrogenation of MBF and TFAP in EP + MBF, KPL + MBF and EP + TFAP mixtures a decrease in hydrogenation rate is observed instead of RE (0.29 < 0.91, 0.24 < 0.73, 0.03 < 0.13) in the same solvent (acetic acid); in the hydrogenation of the other binary mixtures, one of the general laws of the Orito reaction

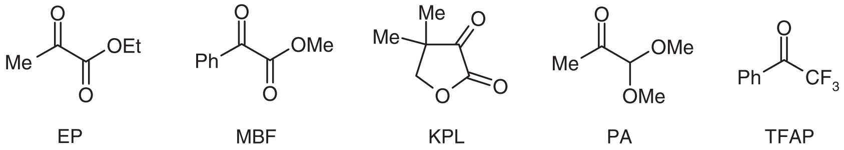

Fig. 1. Activated ketones studied in this research.

Table 1
Experimental data obtained under identical reaction conditions in racemic and chiral hydrogenations of activated ketones[a].

Entry	Substrate	Hydrogenation in toluene			Hydrogenation in AcOH			Refs.
		Conversion (%)			Conversion (%)			
		Racemic	Chiral	ee (%, *R*)	Racemic	Chiral	ee (%, *R*)	
1	EP				20	100	90	[21,22]
2	EP				25	94	91	[25]
3	EP	40	100	78				[26]
4	EP	4.5	51	80				[27]
5	EBF				27	30	77	[23,24]
6	EBF				7	25	83	[25]
7	KPL	50	74		25	72		[28]
8	PA				5	17	85	[25]

Abbreviations: Racemic = racemic hydrogenation, Chiral = chiral hydrogenation.
[a] For the reaction conditions see the cited references.

prevails, *i.e.* $r_C > r_R$; (iii) competitive chiral hydrogenation of EP (entries 6 and 12) is faster than that of MBF (entries 6, 7: 1.72 > 1.12, 0.69 > 0.29) and TFAP (entries 12, 13: 1.2 > 0.17, 0.44 > 0.03), whereas in racemic competitive hydrogenation MBF (entries 6,7) and TFAP (entries 12,13) are hydrogenated faster than the EP (0.78 > 0.16, 0.91 > 0.06 and 0.13 > 0.07); (iv) a similar conclusion can be drawn from the hydrogenation results of the KPL + MBF binary mixture (entries 14 and 15: in chiral hydrogenation 3.92 > 0.24, 3.20 > 0.24, whereas in racemic hydrogenation 0.78 > 0.60, 0.73 > 0.34); hydrogenation of the KPL + MBF system also includes an induction period, namely MBF is not hydrogenated as long as KPL is present in the solution (Fig. 3A; MBF_{Cm}). Unlike in the case of the binary mixtures EP + MBF, EP + TFAP and KPL + MBF, no unexpected phenomena were observed in the other systems studied.

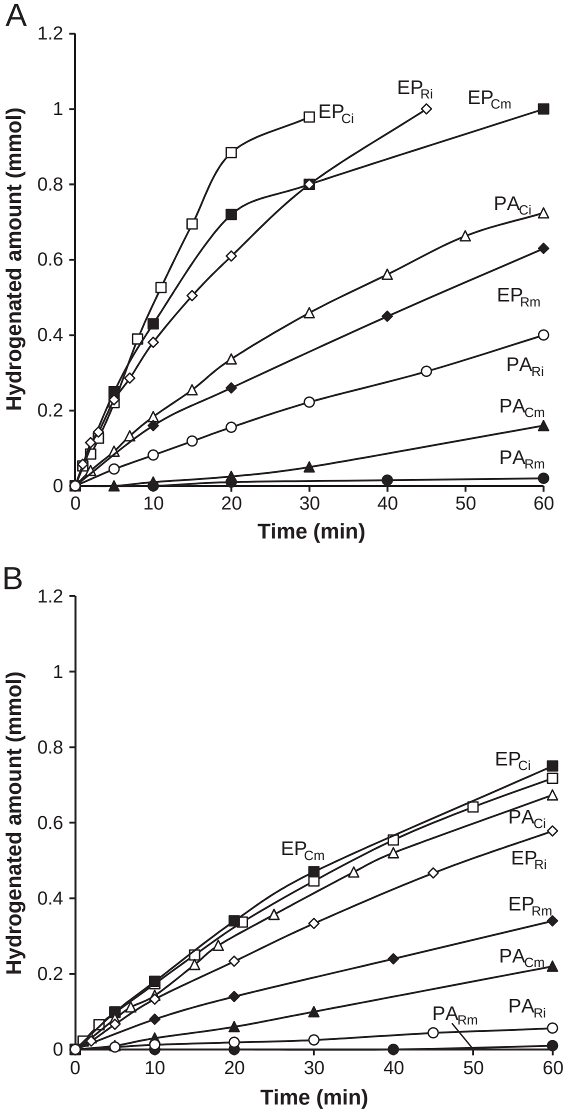

Fig. 2. Amount of hydrogenated substrates in individual hydrogenations and in competitive hydrogenations of EP-PA binary mixture in toluene (A) and in acetic acid (B) (for reaction conditions see subsection *2.2.*); subscript Ci (Ri) = chiral (racemic) hydrogenation of the individual substrate; Cm (Rm) = chiral (racemic) hydrogenation of the binary mixture.

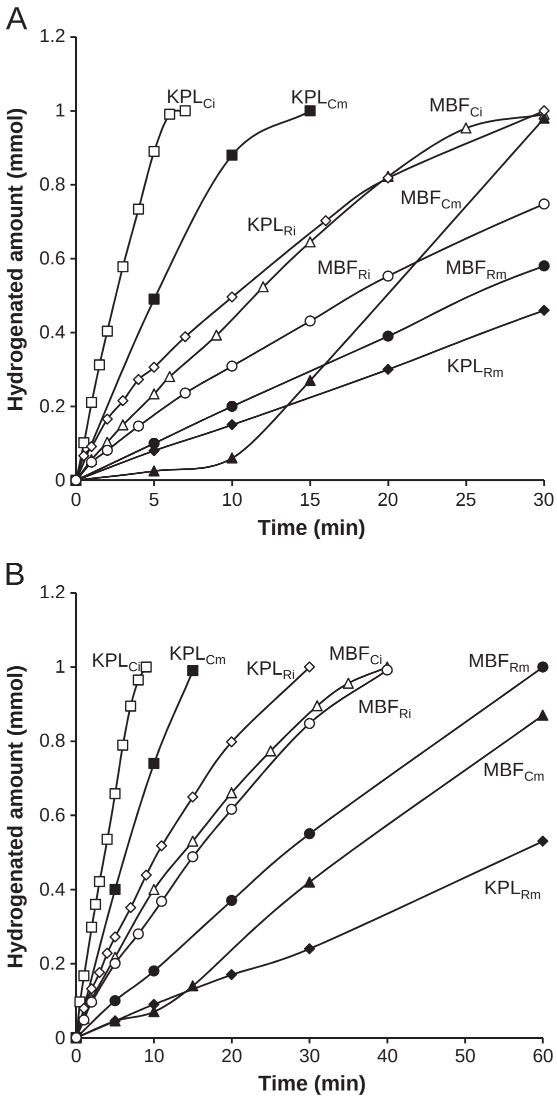

Fig. 3. Amount of hydrogenated substrates in individual hydrogenations and in competitive hydrogenations of KPL-MBF binary mixture in toluene (A) and in acetic acid (B) (for conditions and for abbreviations see Fig. 2.).

The application of the Smith equation has become accepted for the interpretation of the experimental data obtained by competitive hydrogenation: r_{m1}/r_{m2} (relative rate) $= r_{i1}K_1/r_{i2}K_2$[1,9]. From this expression, the relative adsorption coefficients of the starting compounds 1 and 2: $K_{rel} = K_1/K_2$ can be calculated when the values of the rate r_{i1} and r_{i2} are known from individual kinetic measurements: $K_1/K_2 = (r_{m1}/r_{m2})$ x (r_{i2}/r_{i1}). The results calculated from the competitive hydrogenation of binary mixtures are shown in Table 3.

The first and second columns of each hydrogenation in Table 3 present the ratio of reactivities of 1 and 2 (in chiral or racemic

Table 2
Rate of chiral (r_{Ci}) and racemic (r_{Ri}) hydrogenations of individual substrates and of competitive hydrogenations of binary mixtures (r_{Cm1}, r_{Cm2}, r_{Rm1}, r_{Rm2}) and enantiomeric excesses (ee) obtained over the chiral catalyst[a].

Entry	Substrates[b]	Hydrogenation in toluene				Hydrogenation in acetic acid (AcOH)			
		r_{Ci}[c]	ee(%) (*R*)	r_{Ri}[c]	r_{Ci}/r_{Ri}	r_{Ci}[c]	ee(%) (*R*)	r_{Ri}[c]	r_{Ci}/r_{Ri}
1	EP_i[d]	1.88	72	1.35	1.4	0.69	88	0.48	1.4
2	MBF_i[d]	1.93	86	1.32	1.5	1.57	77	1.31	1.2
3	PA_i	0.71	82	0.29	2.4	0.60	95	0.09	6.3
4	KPL_i	8.37	51	2.39	3.5	5.36	39	1.76	3.0
5	$TFAP_i$	0.84	36	0.18	4.8	0.29	30	0.21	1.4
		r_{Cm}	ee(%) (*R*)	r_{Rm}	r_{Cm}/r_{Rm}	r_{Cm}	ee(%) (*R*)	r_{Rm}	r_{Cm}/r_{Rm}
EP + MBF (1 + 2) m.									
6	EP_m[d]	1.72	70	0.16	10.1	0.69	80	0.06	11.5
7	MBF_m[d]	1.12	77	0.78	1.4	0.29	66	0.91	0.3
EP + PA (1 + 2) m.									
8	EP_m	1.72	65	0.52	3.3	0.70	88	0.25	2.9
9	PA_m	0.07	77	0.01	6.6	0.09	96	0.01	9.0
KPL + EP (1 + 2) m.									
10	KPL_m	3.92	40	0.91	4.3	2.33	24	0.52	4.5
11	EP_m	0.51	72	0.10	5.0	0.24	64	0.08	3.2
EP + TFAP (1 + 2) m.									
12	EP_m	1.20	65	0.44	2.7	0.44	55	0.07	6.5
13	$TFAP_m$	0.17	17	0.07	2.4	0.03	5	0.13	0.3
KPL + MBF (1 + 2) m.									
14	KPL_m	3.92	36	0.60	6.5	3.20	34	0.34	9.5
15	MBF_m	0.24	86	0.78	0.3	0.24	57	0.73	0.3
KPL + PA (1 + 2) m.									
16	KPL_m	3.28	23	1.14	2.9	7.44	52	0.68	10.9
17	PA_m	0.04	81	0.03	1.3	0.04	95	0.01	4.0
MBF + PA (1 + 2) m.									
18	MBF_m	1.24	78	0.90	1.4	1.12	68	1.10	1.0
19	PA_m	0.16	87	0.03	4.7	0.15	94	0.001	>100
MBF + TFAP (1 + 2) m.									
20	MBF_m	0.76	87	0.60	1.3	0.42	28	0.46	0.9
21	$TFAP_m$	0.20	22	0.05	4.1	0.05	8	0.05	1.0

[a] Reaction conditions: 25 mg E4759 Pt/Al_2O_3 catalyst, [CD]: 0.8 mM, solvent: 5 mL, H_2 pressure: 0.1 MPa, rt, substrates: 1 mmol, mixtures 1 + 1 mmol, rpm: 900–1000.

[b] Subscript i = hydrogenation of the individual substrate, m = hydrogenation of the binary mixture.

[c] Hydrogenation rates in mmol substrate/mg catalyst min.

[d] These data are taken over from Chem. Commun. 47 (2011) 1551–1552.

individual or competitive hydrogenation), whereas the third column shows the relative adsorption coefficients. The latter calculated data characterize the stabilities of the 1-Pt, 2-Pt and 1-CD-Pt, 2-CD-Pt adsorbed surface complexes, that is the strength of the attachment of intermediate complexes to the catalyst.

The data in Table 3 can be sorted on various criteria for the purpose of drawing certain conclusions. The most conspicuous differences are found among K_1/K_2 and among r_{m1}/r_{m2} values, mainly because values lower than 1 also occur. This means that, in certain cases, the adsorbability of substrate 2 is larger than that of substrate 1 (the others are supplemented with the symbols h: high, l: low and m: medium). For example, binary mixtures 1–8 can be sorted into three groups based on the K_1/K_2 values shown in the four columns: (i) mixtures where in general $K_1 >> K_2$ (entries 2, 6 and 7): in these cases one of the components of the mixture is PA, whose structure and consequently, not only its adsorption mode is significantly different from those of EP, MBF and KPL containing conjugated double bonds, but also the structure of the intermediate complexes responsible for enantiodifferentiation; (ii) mixtures where generally $K_1 > K_2$ (entries 3 and 8),: in these two pairs of compounds (with the exception of one case, *i.e.* hydrogenation of KPL + EP in toluene on unmodified catalyst, where $K_1 >> K_2$) K_1 is hardly any larger than K_2, probably owing to the operation of similar adsorption forces, which are different in the two pairs of compounds (on the one hand, KPL and EP are small molecules as compared to the bulky MBF and TFAP, on the other hand TFAP may also participate in the reaction in the form of dimers and oligomers [40,41]); (iii) mixtures in whose racemic hydrogenation $K_2 > K_1$ (entries 1, 4 and 5): due to the significantly different adsorbabilities of the components of these mixtures, hydrogenations yielded unexpected results, *i.e.* in chiral hydrogenation $K_1 > K_2$, whereas in racemic hydrogenation $K_1 < K_2$. Reaction rate ratios r_{m1}/r_{m2} showed tendencies identical with those of K_1/K_2 in hydrogenations of these three mixtures both over modified and unmodified catalyst.

According to the calculated values in Table 3, in racemic hydrogenations MBF and TFAP are adsorbed on the surface stronger than EP is, whereas in the case of chiral hydrogenations the order of adsorption strengths is reversed. In other words, we assume that CD adsorbs stronger on Pt than the activated ketones (EP, MBF, TFAP). Docking at the remaining surface sites is sterically easier for EP than for the more bulky MBF and TFAP. Due to its phenyl group MBF and TFAP adsorb more strongly than EP on unmodified Pt.

4. Conclusion

The so-called adsorption model for the Orito reaction (cinchona alkaloid/substrate 1/1 adsorbed intermediate complex responsible for enantiodifferentiation and rate enhancement) has by now become universally accepted. No agreement has been reached on the structure of the intermediate complex responsible for enantiodifferentiation [15,42,43] (Fig. 4). In our opinion the structure of intermediate complexes is determined by basic factors such as the chiral modifier, the substrate and the reaction conditions. Utmost caution should be exercised when exclusion of any proposed intermediate is considered. The present results indicated clearly the role of the substrate structure in determining the interactions occurring during the reactions with consequences on the rate and stereochemical outcome of these hydrogenations.

The conclusions drawn from the experimental data of the competitive hydrogenation of activated ketones represent an

Table 3
Calculated relative rates (r_{Ci1}/r_{Ci2} and r_{Cm1}/r_{Cm2}) and relative adsorption coefficients (K_1/K_2) for competitive enantioselective and racemic hydrogenations.

	Binary mixture	Hydrogenation in toluene						Hydrogenation in acetic acid (AcOH)					
		Chiral			Racemic			Chiral			Racemic		
	1 + 2	r_{Ci1}/r_{Ci2}	r_{Cm1}/r_{Cm2}	K_1/K_2	r_{Ri1}/r_{Ri2}	r_{Rm1}/r_{Rm2}	K_1/K_2	r_{Ci1}/r_{Ci2}	r_{Cm1}/r_{Cm2}	K_1/K_2	r_{Ri1}/r_{Ri2}	r_{Rm1}/r_{Rm2}	K_1/K_2
1	EP + MBF	1.0	1.5	1.6 l	1.0	0.1	0.2	0.4	2.4	5.3 h	0.4	0.1	0.2
2	EP + PA	2.6	24.6	9.9 h	4.7	52	11.4 h	1.2	7.8	6.8 h	5.1	25	5.0 h
3	KPL + EP	4.5	7.7	1.7 l	1.8	9.0	5.0 h	7.8	9.7	1.2 l	3.7	6.5	1.9 l
4	EP + TFAP	2.2	7.1	3.1 m	7.5	6.7	0.8	2.4	14.7	5.4 h	2.3	0.5	0.2
5	KPL + MBF	4.3	16	3.8 m	1.8	0.8	0.4	3.4	13.3	3.9 m	1.3	0.5	0.3
6	KPL + PA	11.8	82	6.9 h	8.2	38	5.3 h	8.9	>100	20.3 h	19.6	68	3.7 m
7	MBF + PA	2.7	7.8	2.9 m	4.6	30	5.8 h	2.6	7.7	2.9 m	14.6	>100	16 h
8	MBF + TFAP	2.3	3.8	1.6 l	7.3	12	1.6 l	5.4	8.4	1.5 l	6.3	9.2	1.4 l

For conditions and abbreviations see in Table 2, Chiral = chiral hydrogenation, Racemic = racemic hydrogenation, and h = high, l = low, m = medium.

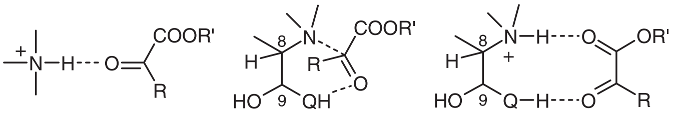

Fig. 4. Proposed intermediate complexes adsorbed on Pt modified by cinchonidine in the enantioselective hydrogenation of activated ketones.

additional, convincing experimental confirmation of the nearly universally accepted mechanism of the Orito reaction, *i.e.* the adsorption model. A similar conclusion was arrived at in studies on the competitive hydrogenation of unsaturated carboxylic acids over Pd-CD chiral catalyst [44].

Important data have been reported on the kinetics of the Orito reaction [20,45,46]. In view of the complexity of the kinetics of heterogeneous catalytic reactions depending on many parameters, further studies are needed, especially in the field of asymmetric reactions. The observations reported in this manuscript also call attention to the significance of further research on the kinetics of competitive chiral hydrogenations (e.g. various instrumental techniques, quantum chemical calculations).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.05.028.

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