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Reversal of the ee in enantioselective hydrogenation of activated ketones in continuous-flow fixed-bed reactor system

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ABSTRACT

A study on the hydrogenation of ethyl pyruvate, methyl benzoylformate and 2,2,2-trifluoroacetophenone over Pt–cinchona alkaloid chiral catalysts and over the "unmodified" catalysts resulted after a cleaning step at 323 K of the chirally modified surfaces in continuous-flow fixed-bed reactor system is presented. According to these investigations the sense of the residual ee observed in the reactions carried out in the absence of modifiers over the catalysts rinsed after the chiral hydrogenations was influenced by the solvent and the structure of the activated ketone, pointing on the effect of these parameters on the structure of the adsorbed intermediate complexes and implicitly on the chiral induction.

1. Introduction

Enantioselective hydrogenation of activated ketones accompanied by the formation of chiral alcohols is the most intensively studied asymmetric heterogeneous catalytic reaction [1,2] (Scheme 1). The diversity of these studies is most probably explained by the fact that enantioselectivities (ee) exceeding 90% could be attained with substrates with a wide structural variety. High enantioselectivities have not only economic but also theoretical significance: researchers in this field are eager to find the explanation for the high ee attainable under mild, undemanding conditions, using relatively simple starting materials. Better understanding of the details of the reaction has been hoped to contribute to the interpretation of other asymmetric transformations and to studies on the origin of chiral induction, with special regard to heterogeneous catalytic reactions. Reviews on the results obtained in studies on the Orito reaction have been published continuously (e.g. in the last four years [3–7]).

The subject of many recently published reports has been the origin of chiral induction [8–18]. However, these reports have not reflected on the unusual results published in 2006 in an article entitled "A new origin for stereo-differentiation in the Orito reaction: Residual chiral induction and enantiomeric excess reversal during piecewise continuous experiments using a chiral fixed-bed reactor" [19]. This title aroused the interest of our research group: the ee values reported were relatively low but, unexpectedly, reversed. In the enantioselective hydrogenation of ethyl benzoylformate (EBF) over Pt/alumina modified by cinchonidine (CD) using continuous-flow fixed-bed reactor system (CFBR), Garland et al. observed that (i) after enantioselective hydrogenation of EBF at 273 K, and after cleaning at 273 K, a *racemic* "unmodified" hydrogenation could be performed, which implies effective desorption of chiral species from the surface in the course of cleaning; (ii) after the same enantioselective hydrogenation at 273 K, and after a cleaning treatment at 323 K, an "unmodified" *enantioselective* hydrogenation was carried out with unexpected reversal of ee; (iii) in similar experiments with ethyl pyruvate (EP) and cinchonine (CN) the ee was again reversed; (iv) in EP hydrogenation over Pt/C and powdered Pt catalysts modified by CD, residual chiral induction was also detected, but retention of the ee direction was observed.

Since the relevant CFBR technique was available in our laboratory [19–21], it seemed expedient to perform similar experiments. In order to reproduce these unexpected results and to supplement them with new data, or, if possible, even to obtain information on the general character of the phenomenon, we studied the enantioselective hydrogenation of EP, methyl benzoylformate (MBF) and 2,2,2-trifluoroacetophenone (TFAP) on Pt catalyst modified by the four parent cinchona alkaloids.

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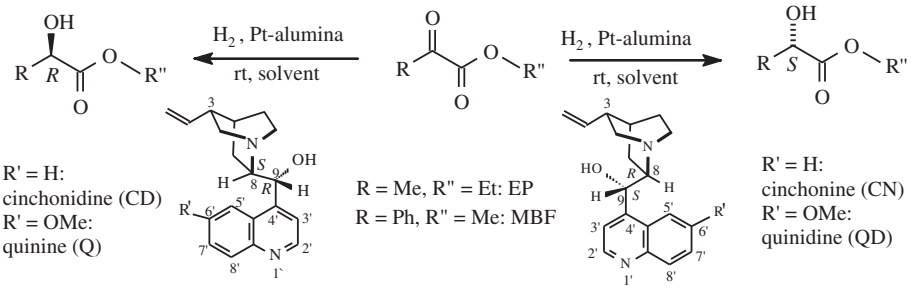


Scheme 1. The Orito reaction.

2. Experimental

2.1. Materials

Cinchona alkaloids — CD, CN, quinine (QN) and quinidine (QD), trifluoroacetic acid (TFA), reagents and solvents were purchased from Aldrich or Fluka, and used as received. EP, MBF and TFAP were distilled using a Vigreaux-column. The catalyst, Engelhard 5% Pt/Al_2O_3 (E4759) was pre-treated in a fixed-bed reactor in H_2 flow at 673 K as previously described [22].

2.2. Hydrogenations in flow system

Continuous hydrogenations were carried in H-Cube high-pressure continuous-flow system. The experimental set-up has been described in detail in our previous publication [17]. A typical series of measurements began with pre-hydrogenation of the catalyst and continued with chiral hydrogenation, followed by desorption of the chiral modifier using a flow of the same solvent at 323 K and by hydrogenation on "unmodified" catalyst (racemic hydrogenation). The measurement series was ended by a second chiral hydrogenation under conditions identical with those of the first one.

2.3. Product analysis

The products were identified by mass spectrometric analysis (HP 6890 N GC–HP 5973 MSD, HP-1MS, 60 m capillary column). Conversions and enantiomeric excesses, $ee\% = |[R] - [S]| \times 100/([R] + [S])$, were determined by gas chromatography (HP 6890 N GC-FID, 30 m Cyclodex-B chiral capillary column) [23,24]. The reproducibility of the results was $\pm 1\%$.

3. Results

Measurement series similar to Garland and coworkers' experiments [19] were carried out to study the enantioselective hydrogenation of EP, MBF and TFAP over Pt/Al_2O_3 catalyst modified by cinchona alkaloids (CD, CN, QN, and QD) in CFBR system. These experiments were performed under similar conditions as used in the hydrogenations of other activated ketones, in a toluene/AcOH (9/1) solvent mixture [17,25] with and without 0.1% (v/v) TFA content and in 2-propanol (2P). Although AcOH is not a favorable component in TFAP hydrogenation [25,26], it was used in our CFBR studies due to its effect to increase the solubility of cinchonas, as in these experiments higher modifier concentrations are required. We used 2P rather than EtOH, because of its lower reactivity with the substrates. It was confirmed already by Orito et al. that there is no significant difference between the effects of these two solvents on the ee [27]. For example, in the hydrogenation of EBF over Pt–CD catalyst the ee values attained were 36.5% in EtOH and 47.3% in 2P (in the hydrogenation of methyl pyruvate 83.2% and 80.6% ees were obtained in these solvents, respectively) [27]. The hydrogenation conditions were selected on the basis of the preliminary experiments and using the earlier published results [19].

3.1. Enantioselective hydrogenation of EP

The majority of the experimental data are summarized in Table 1.

The experimental data clearly show that the catalyst is deactivated by the end of each measurement sequence, with the exception of the series in 2P. During "unmodified" hydrogenation following desorption of the chiral modifier, reversal in ee was observed in toluene/AcOH solvent with one exception (hydrogenation in the presence of TFA) (entries 1–4) as well as in 2P (entries 6 and 7), similarly to hydrogenation in EtOH [19]. The conversions obtained in the enantioselective hydrogenations were higher than in hydrogenations over "unmodified" catalysts.

3.2. Enantioselective hydrogenation of MBF

The characteristic experimental data obtained in the hydrogenations of MBF are summarized in Table 2 and examples for the dependence of conversion and ee versus time on stream are shown in Fig. 1.

In toluene/AcOH solvent mixture, after desorption of the chiral modifiers CD, CN and QN the hydrogenations over the washed "unmodified" catalysts yielded racemic products (entries 1–6), unlike in the case of EP. After desorption of QD reversal of ee was observed (entry 7). The presence of the strongly acidic TFA also led to the formation of racemic products (entry 8). Hydrogenation in 2P, however, produced reversal of ee, similarly to EtOH [19] (entries 9–14, Fig. 1a,b). Decreasing the concentration of MBF affected our basic conclusions inasmuch as at [MBF] = 11 mM the conversions in "unmodified" and in first and second modified hydrogenations were nearly identical (entry 11).

Pt–QN and Pt–QD do not perform well in the hydrogenation of MBF in 2P, however these experiments also gave unexpected results (entries 9, 13, and 14 and Fig. 1c,d). Namely, the first chiral hydrogenation yielded racemic products, whereas both the "unmodified" hydrogenation and the following second chiral hydrogenation produced reversal of ee. In order to reveal the causes underlying this surprising results, we studied the catalyst pre-treatment in the presence of QN, hydrogenations in the absence of oxygen or accompanied by flushing the reaction mixture with air (based on earlier experiences [28]) and the effect of further reductions in MBF concentration (entries 13–17). These experiments pointed to the competition of the modifiers and MBF on the catalyst adsorption sites. MBF present at concentrations significantly higher than the chiral modifier inhibits adsorption of the cinchonas with lower adsorption strength (QN and QD [29,30]), as a consequence the decrease in the number or lack of chirally active sites on the surface leads to the formation of racemic products. The data obtained at [MBF] = 1.1 mM

Table 1
Conversions and ees obtained in the enantioselective hydrogenation of EP in CFBR.[a]

Entry	Modifier	Solvent	[EP] (mM)	Hydrogenations					
				1st modified		"unmodified"		2nd modified	
				C[b]	ee[c]	C	ee	C	ee
1	CD	T/AcOH	45	60	50 *R*	30	7 *S*[e]	40	45 *R*
2	CN	T/AcOH	45	60	40 *S*	20	5 *R*[e]	30	48 *S*
3	QN	T/AcOH	45	85	70 *R*	30	6 *S*[e]	60	67 *R*
4	QD	T/AcOH	45	70	43 *S*	40	5 *R*[e]	45	43 *S*
5	CD	T/AcOH[d]	11	97	90 *R*	33	13 *R*	87	87 *R*
6	CD	2P	11	98	28 *R*	96	2 *S*[e]	98	23 *R*
7	CN	2P	11	90	10 *S*	88	11 *R*[e]	90	5 *S*

[a] Reaction conditions: 40 mg Pt/Al_2O_3, 4 MPa H_2, 293 K, [modifier] = 0.044 mM, in situ desorption of the modifier between the first modified and "unmodified" hydrogenations by rinsing with the solvent at 293 K 60 min, 323 K 60 min and 293 K 30 min, respectively.
[b] Conversion (%).
[c] Enantiomeric excess (%) and absolute configuration of the major enantiomer.
[d] In the presence of 0.1% (v/v) TFA.
[e] Reversed sense of the ee over rinsed catalyst without added modifier.

(entries 18–21) are quite surprising: the formation of racemic products over the "unmodified" catalyst proceeds at a higher rate than does the subsequent second chiral hydrogenation (entries 14, 17, 18, and 21). There may be several reasons for this phenomenon; its interpretation needs further studies, since rate acceleration was occasionally replaced by rate deceleration [31].

3.3. Enantioselective hydrogenation of TFAP

The experimental data obtained in the hydrogenations of TFAP can be seen in Table 3.

It was already clear from our batch reactor and CFBR studies that in the Orito reaction, TFAP does not follow the general rule according to which C8(*S*) C9(*R*) cinchonas (CD and QN) favor the formation of (*R*)-alcohols, whereas C8(*R*) C9(*S*) cinchonas (CN and QD) promote the formation of (*S*)-alcohols in excess [24]. It is also known that in the presence of TFA, *i.e.* in highly acidic medium, hydrogenation over Pt–CN chiral catalyst yields the expected (*S*)-alcohol in excess [32], as also confirmed in the present study (entry 6).

According to these experimental data (Table 3), in the hydrogenations of TFAP in various solvents over the "unmodified" catalyst formed in the course of the desorption of the chiral modifier,

Table 2
Conversions and ees obtained in the enantioselective hydrogenation of MBF in CFBR.[a]

Entry	Modifier	Solvent	Catalyst (mg)	[MBF] (mM)	Hydrogenations					
					1st modified		"unmodified"		2nd modified	
					C[b]	ee[c]	C	ee	C	ee
1	CD	T/AcOH	50	45	99	95 *R*	55	0	99	95 *R*
2	CD	T/AcOH	50	45	98	95 *R*	74	0	87	93 *R*
3[d]	CD	T/AcOH	50	45	90	94 *R*	70	0	96	93 *R*
4	CD	T/AcOH	50	11	100	90 *R*	58	0	88	95 *R*
5	CN	T/AcOH	50	11	97	69 *S*	75	0	85	55 *S*
6	QN	T/AcOH	20	11	40	47 *R*	20	4 *R*	30	46 *R*
7	QD	T/AcOH	20	11	35	3 *S*	23	5 *R*[i]	25	7 *S*
8	CD	T/AcOH[e]	20	11	56	82 *R*	40	0	32	82 *R*
9	CD	2P	20	45	72	55 *R*	44	11 *S*[i]	65	54 *R*
10	CD	2P	20	22	81	51 *R*	63	16 *S*[i]	72	45 *R*
11	CD	2P	20	11	78	55 *R*	76	7 *S*[i]	78	39 *R*
12	CN	2P	20	11	53	25 *S*	55	12 *R*[i]	58	17 *S*
13	QN	2P	20	11	55	0	57	10 *S*[i]	56	15 *S*[i]
14	QD	2P	20	11	50	0	60	6 *R*[i]	50	7 *R*[i]
15	QN[f]	2P	20	11	60	10 *S*[i]	60	5 *S*	58	20 *S*
16	QN	2P[g]	20	11	55	0	55	6 *S*	56	15 *S*
17	QN	2P[h]	20	11	53	0	60	5 *S*	53	13 *S*
18	CD	2P	20	1.1	84	42 *R*	84	0	75	42 *R*
19	CN	2P	20	1.1	69	11 *S*	75	4 *R*[i]	76	9 S
20	QN	2P	20	1.1	80	13 *S*[i]	84	0	88	27 S[i]
21	QD	2P	20	1.1	60	7 *R*[i]	95	0	80	7 *R*[i]
22	QN	2P	20	45		12 *R*	44	5 S[i]	40	3 *R*
23	QD	2P	20	45	27	4 *R*[i]	74	9 *R*[i]	25	7 *R*[i]

[a] Reaction conditions: 4 MPa H_2, 293 K, [modifier] = 0.44 mM, in situ desorption of the modifier between the first modified and "unmodified" hydrogenations by rinsing with the solvent at 293 K 60 min.
[b] Conversion (%).
[c] Enantiomeric excess (%) and absolute configuration of the major enantiomer.
[d] In situ desorption of the modifier 2 hours at 50°C.
[e] In the presence of 0.1% (v/v) TFA.
[f] Catalyst pre-treated with QN.
[g] Using deoxygenated solutions.
[h] Oxygen was bubbled through the solutions before use.
[i] Reversed sense of the ee as compared to expected one based on the configuration of the modifier used in the chiral hydrogenation.

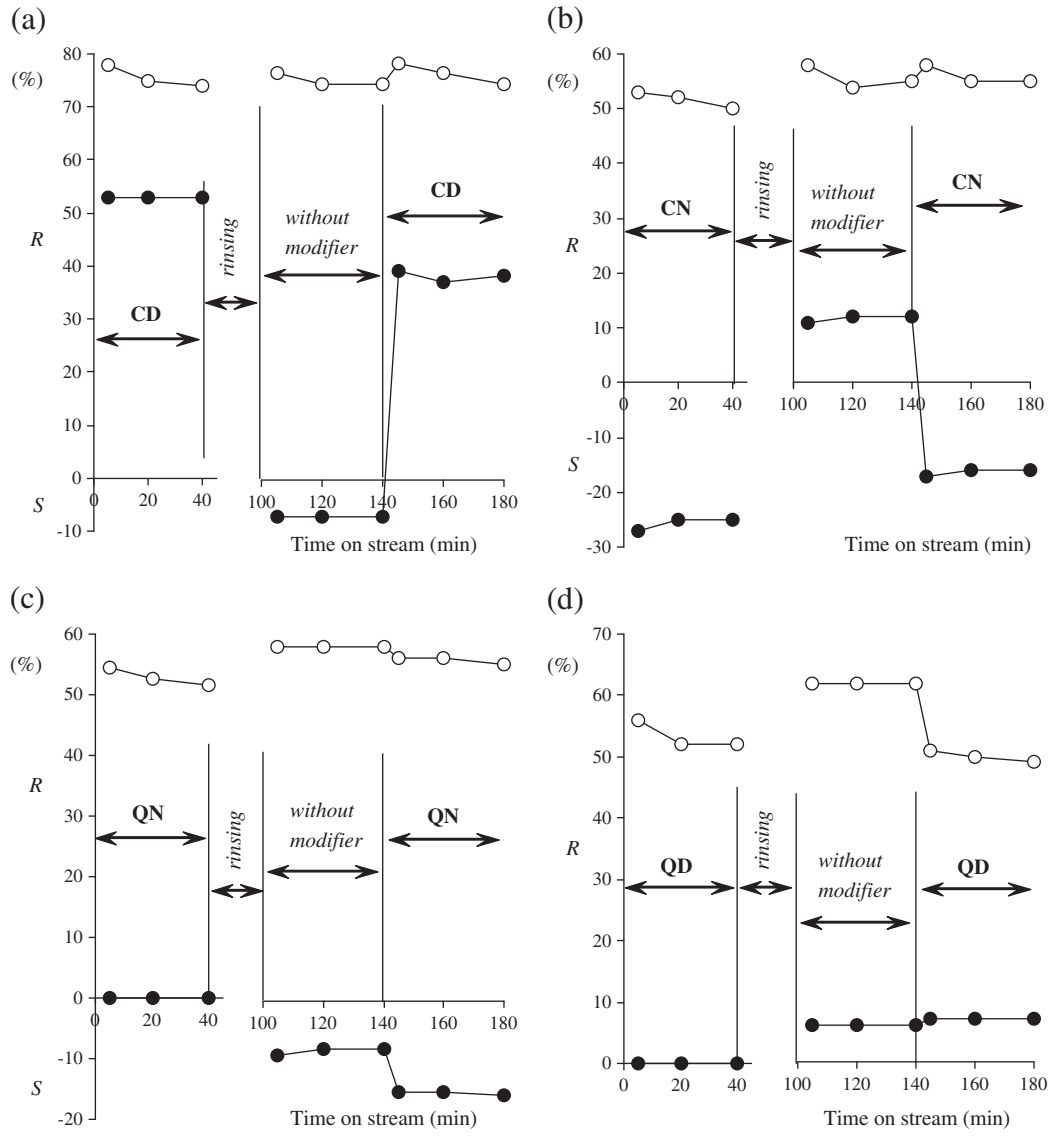


Fig. 1. The conversions (○) and ees (●) as a function of time on stream in the enantioselective hydrogenation of MBF over Pt–CD (a), Pt–CN (b), Pt–QN (c) and Pt–QD (d) catalysts in 2-propanol (see Table 2 for conditions).

formation of the products having reversed sense of the ee as compared with the first chiral hydrogenation was not observed. This means that the conversions of the three activated ketones (EP, MBF, and TFAP) during their enantioselective hydrogenations under nearly identical conditions take significantly different routes.

4. Discussions

4.1. Summary of the new results

Based on the unexpected results reported by Garland et al., we carried out further studies using systematically varied experimental conditions. Experiments were performed using Pt/Al_2O_3 catalyst modified by each of the four parent cinchonas, using EP, MBF and TFAP as substrates in 2P and toluene/AcOH as solvents (occasionally in the presence of TFA). The most important, so far unpublished findings of these experiments were the following: (i) reversal in ee was observed over the so-called "unmodified" catalysts (obtained by previous modification and subsequent desorption of the cinchonas) in the enantioselective hydrogenation of EP in toluene/AcOH solvent mixture, while no change was observed in the sense of ee in the presence of TFA in similar hydrogenations; (ii) similarly to (i), reversal in ee was also observed in 2P over the "unmodified" versions of Pt–CD and Pt–CN catalysts in EP hydrogenation; (iii) "unmodified" hydrogenation of MBF yielded racemic products in toluene/AcOH both in the absence and in the presence of TFA; in 2P, however, reversal in ee was observed; and (iv) in the hydrogenation of TFAP over "unmodified" catalysts the sense of enantioselection was not changed relative to the modified catalysts (Table 4).

Based on the new experimental observations summarized in Table 4 it can be established that the phenomenon recognized by Garland et al. [19] may not be generalized to the enantioselective hydrogenation of activated ketones. Namely, in the case of MBF a significant solvent effect can be observed (there is no effect in toluene/AcOH), and the phenomenon does not manifest at all in the TFAP hydrogenation.

4.2. Interpretation of the residual chiral induction

As regards the interpretation of the phenomenon recognized in the present study, the explanation proposed by Garland et al. based on their pertinent experimental data can be agreed: ee reversal in the

Table 3
Conversions and ees obtained in the enantioselective hydrogenation of TFAP in CFBR.[a]

Entry	Modifier	Solvent	Catalyst (mg)	[TFAP] (mM)	pH_2 (MPa)	Hydrogenations					
						1st modified		"unmodified"		2nd modified	
						C[b]	ee[c]	C	ee	C	ee
1	CD	T/AcOH	100	45	10	54	42 *R*	12	0	20	35 *R*
2	CD	T/AcOH	50	11	40	35	25 *R*	8	0	25	15 *R*
3	CD	T/AcOH	20	11	10	16	18 *R*	3	0	7	18 *R*
4	CD	T/AcOH[d]	50	11	40	30	50 *R*	9	0	13	48 *R*
5	CN	T/AcOH	100	45	10	43	14 *R*	14	2 *R*	24	9 *R*
6	CN	T/AcOH[d]	50	11	40	25	15*S*	7	0	10	10*S*
7	QN	T/AcOH	100	45	10	38	27 *R*	11	2 *R*	22	17 *R*
8	QD	T/AcOH	100	45	10	18	5 *R*	16	0	17	4 *R*
9	CD	2P	50	11	20	71	13 *R*	66	10 *R*	71	13 *R*
10	CN	2P	50	11	20	85	7 *R*	80	2 *R*	73	3 *R*
11	QN	2P	50	11	20	52	0	74	5 *R*	70	0
12	QD	2P	50	11	20	62	6 *R*	77	1 *R*	55	3 *R*

[a] Reaction conditions: 1 MPa H_2, 283 K, [modifier] = 0.44 mM, in situ desorption of the modifier between the first modified and "unmodified" hydrogenations by rinsing with the solvent at 323 K 60 min.
[b] Conversion (%).
[c] Enantiomeric excess (%) and absolute configuration of the major enantiomer.
[d] In the presence of 0.1% (v/v) TFA at 293 K under 4 MPa H_2.

Table 4
Reversal of the ee (*) in the enantioselective hydrogenations of EP, MBF and TFAP over Pt/Al_2O_3 "unmodified" catalysts.

	In toluene/AcOH (9/1)				In 2-propanol				Using TFA[a]	
	CD	CN	QN	QD	CD	CN	QN	QD	CD	CN
EP	*	*	*	*	*	*			–	–
MBF	–	–	–	*	*	*	*	*	–	
TFAP	–	–	–	–	–	–	–	–	–	–

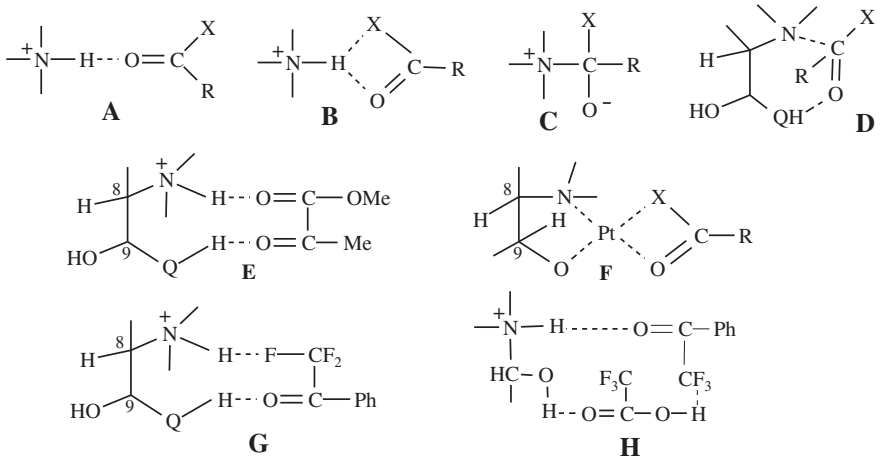
[a] In toluene/AcOH (9/1) in the presence of 0.1% (v/v) TFA.

"unmodified" hydrogenation over Pt/Al_2O_3 can be explained by a superposition of two more or less irreversible modifications of the surface during the 323 K cleaning phase. One is associated with a more or less irreversible change of the Pt surface and a minor ee retention effect, and the other modification is associated with the presence of the alumina support leading to predominant ee reversal effect [19].

Nevertheless, our data pointing to the role of the solvent effect and of the structure of the substrate to be hydrogenated also call attention to the effect of the structure of adsorbed intermediate complexes (ICs) on chiral induction (Scheme 2). Naturally, this also means that chiral induction is dependent (among other factors) on the surface morphology of the metal particles, in other words metal atoms of the surface participate in chiral induction. Irreversible adsorptions detected mainly in the case of CD represent experimentally verified interactions [28,33–36], which may be not only spectators but also relevant species [37].

There are no experimental data published on the examination of the quantity and quality of the organic residues adsorbed irreversible (chemisorbed) on the surface of the catalysts used in CFBR experiments. For this reason elemental analysis of the catalyst was carried out to obtain information on the chemisorbed organic materials. The Pt–CD catalyst used in the hydrogenation of MBF in 2P after cleaning 1 h at 323 K contained 1.50 wt.% C and 0.06 wt.% N (similarly as observed previously by examining the catalyst used in batch reactor [38]). Since the only source of N is the modifier and the commercial CD contains up to ~8% QD the chemisorbed compounds can be attributed to CD, QD and their decomposition products. Thus, one could suppose that the reason of the inversion in the ee is the QD present in the commercial CD, as due to its "tilted" adsorption QD can be hydrogenated slower than the flatly adsorbed CD. However, the results presented in Fig. 1d contradicted this assumption.

However, the hydrogenated derivatives of CD are desorbed easier from the surface [31,39–42]. According to our experimental results



Scheme 2. Proposed intermediate complexes adsorbed on Pt in the enantioselective hydrogenation of EP, MBF and TFAP (X = activating group, R = Me or Ph, Q = quinolinyl): **A** [3,18,39–41], **B** [3,18,39–41], **C** [42], **D** [44], **E** [43], **F** [28], **G** [11,24], **H** [24,45].

during the reductive regeneration of the catalyst at 323 K the chemisorbed cinchonas cannot be removed (see section 2.2, Tables 1–3). When the solvent contained AcOH one may not neglect the formation from the Pt/Al_2O_3 of acetates and other compounds identified by ESI-MS [22,44–46] and their effect on the hydrogenation. The continuous reconstruction of the surface of the Pt/Al_2O_3 under the conditions of the Orito reaction [28,33–35,43,47–49] may affect the sense of the enantioselection, which besides the unexpected experimental results presented in Fig. 1c,d makes necessary further investigation of the phenomenon.

5. Conclusion

A large variety of hypothetic structures of surface ICs potentially responsible for enantiodifferentiation (ED) are shown in Scheme 2 for EP, MBF and TFAP [3,11,18,24,28,50–57]. In addition to kinetic studies, various spectroscopic techniques have also been successfully applied to study the IC structure and the mechanism of the Orito reaction [11–13,39,40], particularly to find explanations for the unexpected inversions detected in these systems (see review in [8]).

Direct experimental identification of the ICs presented in Scheme 2 under the conditions of the Orito reaction is at present impossible. Complexes **A** and **B**, and to a lesser extent complex **C** are generally accepted for the interpretation of the enantioselective hydrogenation of activated ketones in protic solvents. In the case of non-protic solvents, complexes of type **D** cannot be excluded either (in addition to **A** and **B**). The role of complexes **E**, **G**, and **H** in ED has been proposed recently. Type **F** complexes may develop on the most active surface atoms (kink and adatom) by irreversible adsorption (chemisorption). Pt–cinchona complexes produced by chemisorption may have an important role in the phenomenon described in ref. [19]. They are converted to products on surface sites not identical with the original ones, formed after desorption at 323 K, via ICs with structures determined by the structure of the ketone to be hydrogenated.

As a final note: what the authors defined as “a new origin for stereo-differentiation in the Orito reaction” in [19] is indeed a new phenomenon; in our opinion, however, it can hardly be considered to be an Orito reaction, since hydrogenation takes place after desorption of the chiral modifier at 323 K, *i.e.* in the absence of the modifier.

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