Investigation of the Influence of pH on the Catalytic Asymmetric Hydrogenation in Aqueous Micellar Media

Ingrid Grassert,[a] József Kovács,[b] Hans Fuhrmann,[a] Günther Oehme[a,*]

[a] Institut für Organische Katalyseforschung an der Universität Rostock e. V., Buchbinderstraße 5 – 6, 18055 Rostock, Germany
Fax (+49)-381-46693-24, guenther.oehme@ifok, uni-rostock.de
[b] Research Group of Homogeneous Catalysis, Hungarian Academy of Science, University of Debrecen, P.O. Box 7, Debrecen, 4010, Hungary

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Dedicated to Prof. Bernhard Lücke on the occasion of his 65th birthday

Abstract: The influence of pH on the asymmetric hydrogenation of α-amino acid precursors was investigated in the presence of different types of amphiphiles in water as medium. Non-ionic, cationic and zwitterionic amphiphiles gave optimal results with respect to activity and enantioselectivity between pH 2 and pH 5. Anionic amphiphiles were effective in the range from pH 2 up to pH 8 (sometimes pH 9). Comparable results were obtained with cationic and anionic polymeric micelles. Some relationships exist between CH/CD exchange in D_2O and the pH dependence of the hydrogenation. As a practical consequence the pH in micellar hydrogenation systems should be chosen between pH 2 and pH 4.

Keywords: amphiphiles; asymmetric catalysis; hydrogenation; micelles; pH-dependence

Introduction

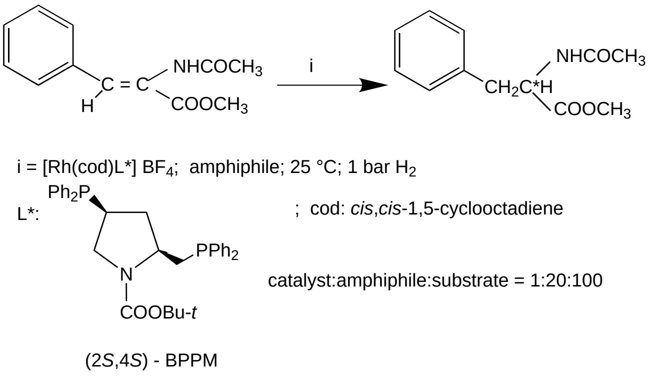
The importance of water as medium for homogeneously catalyzed reactions is increasing as a way to environmentally benign processes.[1] Another aspect is the convenient separation of product and catalyst in an aqueous two-phase system.[2] As a pioneering work the hydroformylation realized by Ruhrchemie-Rhone Poulenc should be mentioned.[3] Classical aqueous phase reactions are hydrogenation,[4] hydroformylation, and a step in the vitamin E synthesis with C-C-bond formation.[5] Catalytic oxidation reactions[6] are in a preparatory industrial phase. For several organic syntheses water as medium has brought about improvements in activity and selectivity.[7] Water is the favoured solvent in the concept of Green chemistry.[8]

Catalyzed processes like hydroformylation and hydrogenation occur via transition metal hydrides and show dependence on the pH. Smith et al.[9] observed an influence of pH on the conversion of the olefin in the hydroformylation of octene catalyzed by cobalt complexes with water-soluble ammonium alkyl(diphenyl)-phosphines as ligands. Kinetic investigations of the rhodium complex-catalyzed reaction were reported by Deshpande et al.[10] and already by Cornils et al.[11] All authors agree that the reaction is less effective in a neutral range than in a slightly basic range (pH 10), independent of the hydrophilic group in the complex.[12]

Joó and coworkers described in a series of papers the pH-dependence of hydrogenation reactions. The favoured hydrophilic ligand was the monosulfonated triphenylphosphine (tppms).[13] In the case of Ru(II) catalysts the authors were able to investigate a pH-dependent equilibrium of mono- and dihydrides with different regioselectivities towards α,α′-unsaturated aldehydes.[14,15] Both hydride structures could be detected by NMR.[16] Much more difficult was the proof in the rhodium(I)-catalyzed hydrogenation reaction[17] although the dihydride and even the monohydride are steps in the hypothetical mechanism.[18] Recently, Joó et al.[19] characterized the intermediates by a reaction of $[RhCl(tppms)_3]$ and *trans*-$[RhCl(CO)(tppms)_2]$ with hydrogen.

We are interested in the rhodium-catalyzed asymmetric hydrogenation of α-amino acid precursors in aqueous micellar media as displayed in Scheme 1.

The presence of micelle-forming amphiphiles gave significant effects on activity and enantioselectivity.[20,21] These effects are connected with the formation of the micelles.[22] Amphiphiles have also an influence on the CH/CD exchange in α-position within the hydrogenation, but this seems to be a non-micellar effect.[23] In this communication some investigations are reported about the pH-dependence of activity and enantioselectivity in the presence of different amphiphiles in an aqueous micellar medium.



Scheme 1. Asymmetric hydrogenation of unsaturated amino acid derivatives in aqueous-micellar medium.

Results and Discussion

In contrast to a homogeneous hydrogenation with water-soluble rhodium(I)-phosphine complexes the micellar method applies water-insoluble complexes and substrates which can be solubilized in colloidal assemblies. That means the concentration of catalyst and reactant (the unsaturated substrate and hydrogen) is higher than in the bulk water phase.[24] The same situation can be expected in the case of the concentration of protons and hydroxyl anions by use of anionic or cationic amphiphiles in water at different pH's. The acidity or basicity on the surface of the micelle should be higher than in the surrounding water phase.[25] As a result, the pH of the bulk water is only approximately a measure of the pH in the micellar region. To avoid side effects in our hydrogenation system, we decided to work in a buffer-free system at constant pH's. (The influence of buffers on nucleophilic reactions in micelles is mentioned by Ruasse et al.[26])

The hydrogenation apparatus contained a glass electrode and a mercury(I) sulfate reference electrode to indicate the pH and two automatic burettes with 0.18 M KOH and 0.18 M $HClO_4$ to compensate deviations from the pH. The glass electrode was adjusted with two buffer solutions of pH 4.002 and pH 7.002 at 20 °C and a constant pH could be regulated automatically.

Titration under argon and alternatively under hydrogen within the hydrogenation process gave almost similar titration curves. Obviously, there is no production of protons during the hydrogenation which would be in accordance with a dihydride mechanism described by Halpern and coworkers.[27] An alternative monohydride mechanism is given in Ref.[18] and can occur in presence of a base, e.g., NEt_3.

In all hydrogenation experiments the mixture was deaerated with argon and after that the argon replaced by hydrogen. During the deaeration procedure (alternation of vacuum and gas) the electrodes were removed and stored in water. On insertion of the electrodes into the reaction mixture under hydrogen atmosphere the electrodes were equilibrated for 1–2 min due to stirring and display a pH > 2 (dependent on the composition of the mixture and the choice of amphiphile).

Table 1 summarizes results with different types of amphiphiles (anionic, cationic, zwitterionic and nonionic) to investigate their influence on activity (here given as time of the half amount of the stoichiometrically consumed hydrogen) and on enantioselectivity of the hydrogenation at different pH's. All data were obtained above the critical micelle concentration (CMC) with a cationic Rh(I)-BPPM complex as catalyst.

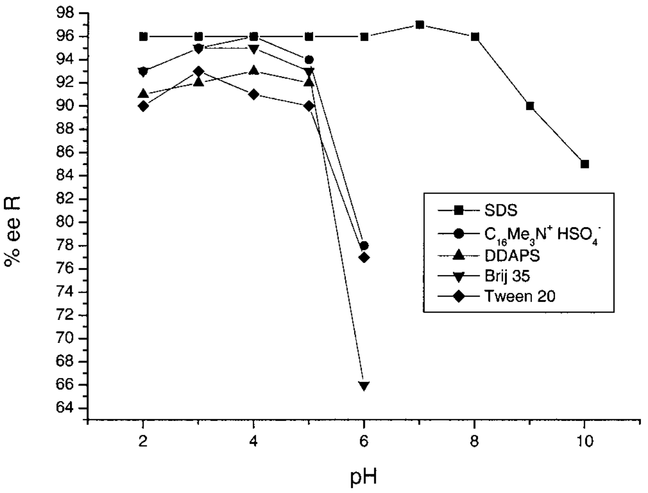


Figure 1. Influence of pH on the enantioselectivity of the asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate in presence of different amphiphiles above the CMC (conditions see Table 1).

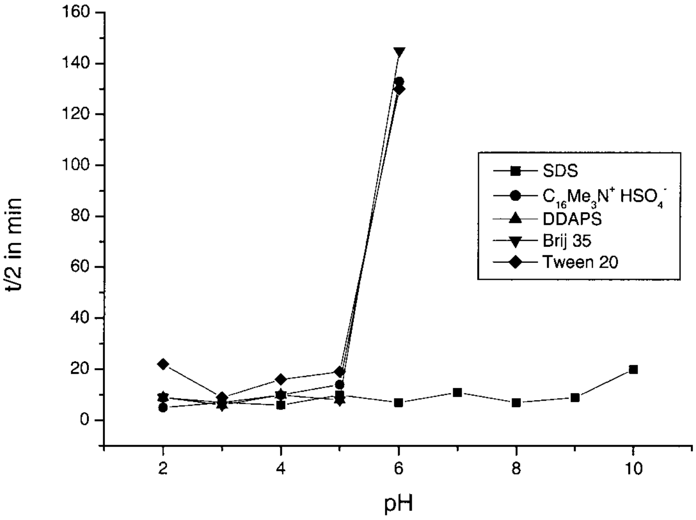


Figure 2. Influence of the pH on the activity of the asymmetric hydrogenation of methyl (Z)-α-acetamidocinnamate in aqueous micellar media in presence of different amphiphiles (conditions see Table 1).

Table 1. Influence of pH on enantioselectivity and activity of the asymmetric hydrogenation of methyl (*Z*)-α-acetamido-cinnamate (Ae) in the presence of different amphiphiles above the CMC {Ae (1.67 mmol) + H_2 (0.1 MPa) catalyzed by [Rh(cod)$_2$]BF_4 + BPPM (0.017 mmol), at 25°C in water (25 mL)}.

Amphiphile	CMC [mol/L]	Rh:Amphiphile	pH	t/2 [min]	% ee *R*	Remarks[a]
SDS	8.1×10^{-3}	1:20	2	9	96	
			3	7	96	
			4	6	96	
			5	10	96	
			6	7	96	
			7	11	97	
			8	7	96	(Rh↓)[b]
			9	9	90	Rh↓
			10	20	85	Rh↓
$C_{16}Me_3N^+$ HSO_4^-	6.0×10^{-4} [c]	1:20	2	5	93	
			3	7	95	
			4	10	96	
			5	14	94	
			6	133	78	Rh↓
DDAPS	1.2×10^{-3}	1:20	2	9	91	
			3	6	92	
			4	10	93	
			5	8	92	Rh↓
			6	–	–	Stopped before t/2
Brij 35	1.7×10^{-5}	1:20	2	9	93	
			3	6	95	
			4	10	95	
			5	8	93	
			6	145	66	
Tween 20	5.9×10^{-5}	1:20	2	22	90	
			3	9	93	
			4	16	91	
			5	19	90	
			6	130	77	

SDS: sodium dodecyl sulfate; $C_{16}Me_3N^+$ HSO_4^-: hexadecyltrimethylammonium hydrogen sulfate; DDAPS: 3-(dodecyldimethylammonio) propanesulfonate; Brij 35: polyoxyethylene(23) dodecyl ether; Tween 20: polyoxyethylene(20) sorbitan monododecanoate.

[a] The yellow dispersion became grey due to formation of colloidally stabilized rhodium particles. In some cases of these observations activity and/or enantioselectivity decreased. In our experience the hydrogenation activity of rhodium particles could not compete with that of the complex.

[b] Not unambiguous.

[c] CMC not available, used from $(C_{16}Me_3N^+)_2$ SO_4^{2-}.

As can be seen in Table 1 and in Figures 1 and 2 there is a relationship: a high activity causes a high enantioselectivity.

The results were obtained stepwise from (constant) pH to pH. The largest range (pH 2 – pH 9) of an almost constant activity and enantioselectivity was observed with SDS as amphiphile. The cationic amphiphile $C_{16}Me_3N^+$ HSO_4^-, the non-ionic amphiphiles Tween 20 and Brij 35, and also the zwitterionic amphiphile DDAPS yielded high activities and enantioselectivities between pH 2 (the lowest investigated pH) and pH 5. We suppose that the measured pH's are real values of the bulk water but we cannot exclude an influence of the amphiphiles due to an adsorption on the surface of the glass electrode.

To make sure of the exceptional position of SDS we employed some more anionic amphiphiles in our investigations. The results with SDS collected in Table 1 are arranged in Table 2 together with structurally comparable amphiphiles directed to decreasing CMC's.

Both amphiphiles with shorter alkyl tails, SDeS (sodium decyl sulfate) and SUS (sodium undecenyl sulfate), are only active at higher concentrations (> 20 mol %) than those with longer tails (SDS, SHS, Na^+ $C_{12}SO_3^-$ and Na^+ $C_{16}SO_3^-$). In accordance with earlier observations, the formation of micelles seems to be necessary for a successful asymmetric hydrogenation. A comparison of the lower concentration of SUS with the higher concentration (Rh:amphiphile = 1:50) point to a dependence of the reaction rate on the CMC (the

Table 2. Investigation of the correlation of the pH and different anionic amphiphiles and their influence on the asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate in aqueous media (conditions, see Table 1).

Amphiphile	CMC [mol/L]	Rh:Amphiphile	pH	t/2 [min]	% ee *R*	Remarks[a]
SDeS	3.3×10^{-2}	1:50 (1:30)	2	2 (4)	94 (93)	
			3	3 (4)	94 (92)	
			4	4 (5)	94 (92)	
			7	4 (32)	93 (87)	Rh↓ (Rh↓)
SUS	3.0×10^{-2}	1:50 (1:20)	2	4 (18)	94 (89)	
			3	5 (8)	94 (92)	
			4	5 (24)	94 (90)	
			5	4 (30)	94 (98)	
			6	5 (49)	93 (87)	
			7	5	93	
SDS	8.1×10^{-3}	1:20	2	9	96	
			3	7	96	
			4	6	96	
			6	6	96	
			8	7	96	
			9	9	90	Rh↓
			10	20	85	Rh↓
SHS	4.5×10^{-4}	1:20	2	3	94	
			4	3	94	
			6	6	94	
			7	8	92	Rh↓
			8	11	90	Rh↓
$Na^+C_{12}SO_3^-$	9.3×10^{-3}	1:20	2	4	95	
			4	5	95	
			7	4	95	
			8	8	92	
			9	189	76	23% educt
$Na^+C_{16}SO_3^-$	1.8×10^{-3} [b]	1:20	2	5	94	
			4	13	91	
			5	7	92	
			6	18	91	
			7	124	81	

SDeS: sodium decyl sulfate; SUS: sodium undecenyl sulfate; SDS: sodium dodecyl sulfate; SHS: sodium hexadecyl sulfate; $Na^+ C_{12}SO_3^-$: sodium dodecanesulfonate (for SDeS and SUS are values for lower concentrations in parentheses).

[a] See footnotes of Table 1.

[b] At 20 °C.

concentration reaches at 0.835 mmol in 25 mL water, just the CMC). Obviously, the optimum seems to be given with SDS, which is active up to pH 9.

As a result of earlier investigations[28] we believe that the reaction occurs inside of the micelle in the "palisade layer"[29] near the transition of the hydrophilic head group to the hydrophobic core. The organic substrate and the hydrogen can penetrate the anionic surface of the micelle whereas the cationic rhodium complex should interact with the sulfate or sulfonate anion in the headgroup, which allows a switching to the reactants. Going back to Table 1, cationic, zwitterionic and non-ionic micelles are only active in a weakly acidic range and probably the cationic rhodium complex competes here with surface-bound water molecules. Possibly, the water content is higher in the interior of these micelles.[30]

What is the reason for the outstanding role of SDS in Table 2? In accordance with results of the α-CH/CD exchange of methyl (*Z*)-α-acetamidocinnamate within the hydrogenation in deuterium oxide as medium in presence of amphiphiles,[23] it is probable that the rhodium complex cation combines with a free long-chain sulfate or sulfonate anion and can more easily penetrate the surface of the micelle. In fact, we observe besides the dependence on the CMC (in case of SDeS and SUS) for long-chain sulfates and sulfonates ($> C_{12}$) also a pH-dependence with respect to the availability of sulfate or sulfonate anions in the bulk water phase. The concentration of free ions decreases with the increase of the chain length and the pH range of high effectivity is for SHS smaller than for SDS and for $Na^+ C_{16}SO_3^-$ smaller than for $Na^+ C_{12}SO_3^-$. To check this explanation, we added a small amount of SDS (only 2 mol %) to

Table 3. Influence of small amounts of SDS on the pH-effective range of enantioselectivity and activity in the asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate (conditions see Table 1).

Amphiphiles	Rh:Amphiphiles	pH	t/2 [min]	% ee *R*	Remarks[a]
Brij-35	1:20	2	10	93	
SDS	1:2	2	-	64	31% conversion
Brij-35 + SDS	1:20:2	4	6	94	
	1:20:2	5	6	95	
	1:20:2	6	9	90	(Rh↓)[b]
	1:20:2	7	41	69	Rh↓
	1:20:2	8	171	71	65% conversion
SHS	1:20	8	11	90	Rh↓
SHS + SDS	1:18:2	8	5	94	
	1:18:2	9	654	79	Rh↓
DDAPS	1:20	6	–	82	45% conversion
DDAPS + SDS	1:20:2	6	67	89	89% conversion

For abbreviations of the amphiphiles, see Tables 1 and 2.

[a] See footnotes of Table 1.

[b] Not unambiguous.

Table 4. Influence of the pH on the asymmetric hydrogenation of methyl (*Z*)-α-acetamidocinnamate in the presence of polymerized amphiphiles in aqueous micellar media (conditions, see Table 1).

Amphiphile[a]	pH	Rh:Amphiphile	% ee *R*	t/2 [min]	Remarks
M 30/1	2	1:20	93	10	94% conversion
	3	1:20	93	7	
	4	1:20	93	9	
	5	1:20	90	112	68% conversion
M12 (SUS)	2	1:20 (1:50)	88 (94)	6 (4)	
	3	1:20 (1:50)	92 (94)	8 (5)	
	4	1:50 (1:50)	95 (94)	5 (5)	
	5	1:50 (1:50)	93 (94)	5 (4)	
	6	1:50 (1:50)	92 (94)	5 (5)	
	7	1:50 (1:50)	89 (93)	8 (5)	95% conversion
	8	1:50 (1:50)	94 (91)	12 (6)	
	9	1:50 (1:50)	91 (89)	51 (12)	82% conversion (95% conversion)

[a] M30/1: polyethyleneimine reacted with $C_{12}H_{25}OSO_3H$; M12: poly(sodium undecenyl sulfate); SUS: sodium undec-10-enyl sulfate (values in parentheses).

selected amphiphiles with a very low CMC. The SDS should mainly appear in the bulk water phase, because the composition of mixed micelles depends on the ratio of CMC's.[31] The results are summarized in Table 3. Obviously, we observe an improvement of the pH effect in all examples. SDS plays here possibly the role of a phase-transfer reagent.

The extreme case of monomer-free amphiphilic systems should be demonstrated in Table 4 with polymeric and polymerized micelles as supports. M30/1 is a micelle-forming polymer obtained from polyethyleneimine and sulfuric acid monododecyl ester and M12 is sodium ω-undecenyl sulfate polymerized in water above the CMC and purified by membrane filtration. Both polymers are described in Ref.[32]

The results are almost similar to those with cationic and anionic micelles formed by monomeric amphiphiles: M30/1 acts as cationic micelle and promotes activity and enantioselectivity of the hydrogenation between pH 2 and pH 4 and the polymerized sulfate M12 promotes between pH 2 and pH 9. M12 acts comparably to SDS but we chose here partly a higher concentration to be comparable with the assemblies of the monomer SUS. The similarity of the effects with supramolecular and macromolecular micelles shows that here a dynamic phenomenon is not the decisive effect (association-dissociation of the assembly).

Table 5 gives a comparison of the pH influence with SDS and $C_{16}Me_3N^+$ HSO_4^- on the CH/CD exchange in D_2O. In both cases there is an interconnection between enantioselectivity, activity and isotopic exchange. An increasing exchange is connected with increasing pH and decreasing enantioselectivity and activity. Anionic amphiphiles like SDS lose the inhibition on CH/CD

Table 5. H/D-exchange in the hydrogenation of methyl α-acetamidocinnamate in D_2O (15 mL) at different pH's (conditions, see Table 1).

pH	SDS			$C_{16}Me_3N^+$ HSO_4^-		
pH	% ee *R*	t/2 [min]	CH/CD-exchange % CD	% ee *R*	t/2 [min]	CH/CD-exchange % CD
2.0	93	4	4	96	4	23
3.0	92	8	6	95	7	21
4.0	92	7	9	94	12	27
5.0	93	4	9	89	35	27
6.0	91	6	9	77	86	30
7.0	91	18	9	–	–	–
8.0	89	18	13 (Rh↓)[a]	–	–	–
9.0	76	36	20 (Rh↓)	–	–	–

[a] See footnotes of Table 1.

exchange[23] above pH 8 which is even the limit of the promotion of the activity and enantioselectivity.

It seems that the concept of a "closed" micelle with a headgroup, a "palisade layer" and a hydrophobic core is optimally realized in anionic micelles. This was also concluded in a paper by Papp et al.[33] investigating the CH/CD exchange in presence of Tween 80 or SDS. Probably the penetration of water into the "palisade layer" of SDS micelles is lower than in the cases of cationic, zwitterionic and non-ionic micelles. A final explanation of this phenomenon needs more experiments. Our understanding of catalyzed reactions in the interior of micelles is just at its beginning.[34] The consequence for practical use of micellar systems in the enantioselective hydrogenation of amino acid precursors is unambiguous: only anionic amphiphiles are suitable for pH's above 6.

Conclusions

Different types of micelle-forming amphiphiles promote activity and enantioselectivity in the asymmetric hydrogenation of methyl (Z)-α-acetamidocinnamate in aqueous systems in dependence on the pH of the reaction mixture and on the type of amphiphile. Anionic amphiphiles are very active in a large pH-range from 2 to 9, but cationic, non-ionic and zwitterionic amphiphiles work well only in a small pH range from 2 up to 5. The reason for the decrease in activity and enantioselectivity seems to be a loss of permeability of the micelle for the rhodium complex by changing the charge on the surface. Added SDS can fulfill a phase-transfer function in small ranges. Polymeric amphiphiles activate this reaction in dependence on the charge in a comparable manner. In case of the hydrogenation in D_2O as medium a dependence of H/D exchange on the pH could be observed. At high pH's the activity and enantioselectivity decrease and the H/D exchange increases. Anionic amphiphiles promote activity and enantioselectivity over a large pH range and inhibit in this range the H/D exchange.

An important consequence should be a suitable combination of pH and the type of surfactant for the hydrogenation in aqueous micellar media.

Experimental Section

General Procedures

The enantiomeric excess of the products was determined by GLC on a Hewlett-Packard chromatograph 5880 A equipped with a 10 m capillary column (column ID: 0.2 mm), fused silica covered with XE-60-L-*N*-*tert*-butylvalinamide synthesized in our laboratory [FID; split 1:60, 150 °C isotherm; retention times: 4.33 min (*R*)-enantiomer; 4.74 min (*S*)-enantiomer ($\alpha = 1.9$; baseline separation) carrier gas: argon, 1 mL/min].

NMR spectra were recorded on a Bruker AC 250 instrument. Chemical shifts of ^1H are reported in parts per million and referenced to Me_4Si as standard.

Materials

Most detergents and BPPM were purchased from commercial sources and used as obtained. Sodium dodecyl sulfate, sodium decyl sulfate, sodium hexadecanesulfonate and hexadecyl trimethylammonium hydrogen sulfate were purchased from Fluka, Switzerland, BPPM and sodium dodecanesulfonate from Merck, Germany, Tween compounds and sulfobetaines were from Sigma, USA, Brij 35 was from Aldrich, USA. Syntheses of the amphiphiles M30/1, M12 and SUS are reported elsewhere.[32]

Hydrogenation under Conditions of pH-Potentiometric Measurements

Hydrogenation was performed by an isobaric method at 25 °C under air-free conditions. Deaerated H_2O (D_2O) (25 mL), surfactant (as a rule 0.334 mmol), $[Rh(cod)_2]BF_4$ (6.68 mg, 0.017 mmol), BPPM (11.69 mg, 0.017 mmol) and methyl (*Z*)-α-acetamidocinnamate (365.7 mg, 1.67 mmol) were placed in the double-walled, deaerated hydrogenation flask and stirred for 15 minutes (polymeric micelles need an equilibration time of at least 2 h). The experimental setup for the pH-potentiometric measurements includes this reactor equipped with inlets for Ar or H_2 and for KOH (about 0.18 M) and $HClO_4$ (about 0.18 M) solutions, a magnetic stirrer and a Radiometer ABU 93 Triburette controlled by a PC. The pH was adjusted with $HClO_4$ or KOH to the required value in the 2 – 10 range. The pH changes can be monitored over time. At the desired pH the stirring was stopped and in the reaction bottle the argon replaced by hydrogen at atmospheric pressure. Both electrodes, the glass electrode pH G201-7 and the reference electrode REF 601 [mercury(I) sulfate], were removed during dearations or gas changing processes.

The control software was PHGER.BAS. This is a Quickbasic programme and it can be run by the PHGER.BAS that opens the Quickbasic (QBASIC.EXE) The pH measurements were done continuously. The base and acid solutions were stored under argon. The electrode calibrations was made with buffer solutions pH 4.002 (20 °C) and 7.002 (20 °C).

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