Journal of Applied Electrochemistry **34**: 127–136, 2004.

Electrocatalytic hydrogenation of alkyl-substituted phenols in aqueous solutions at a Raney nickel electrode in the presence of a non-micelle-forming cationic surfactant

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Received 28 June 2003; accepted in revised form 18 August 2003

Key words: alkylphenols, electrocatalytic hydrogenation, Raney nickel electrode, surfactant adsorption

Abstract

The electrocatalytic hydrogenation (ECH) of 2,6-dimethylphenol and 2-*tert*-butylphenol was performed at RaNi cathodes in aqueous buffers containing various amounts of didodecyldimethylammonium bromide (DDAB). Without surfactant, 2,6-dimethylcyclohexanol, 2-*tert*-butylcyclohexanone and 2-*tert*-butylcyclohexanol were obtained, at 65 °C, with very low yields. The surfactant effect on the yields, the selectivity of the reaction and the diastereoisomeric composition of alkylcyclohexanols produced was studied in acidic and basic solutions in relation to the substrate adsorption. At pH 9 the efficiency of the hydrogenation reaction was significantly improved by low amounts of DDAB, which led to an increase of the alkylcyclohexanols formation. In particular, *cis*-2-*tert*-butylcyclohexanol was obtained with a high diastereoselectivity.

1. Introduction

Electrocatalytic hydrogenation (ECH) at Raney nickel (RaNi) cathodes constitutes a useful method widely used for the hydrogenation of various unsaturated compounds under mild conditions [1]. The chemisorbed hydrogen (H_{ads}) generated *in situ* at low overpotential by electroreduction of hydronium ion (or water) (Reaction 1) reacts with the adsorbed organic substrates (Y=Z) (Reactions 2–4) under normal pressure and low temperature (<100 °C). These mild conditions prevent (or strongly limit) side reactions usually encountered in chemical catalytic hydrogenation.

$$H_3O^+(H_2O) + e^- \rightleftharpoons H_{ads} + H_2O(OH^-) \tag{1}$$

$$Y{=}Z \rightleftharpoons Y{=}Z_{ads} \tag{2}$$

$$Y{=}Z_{ads} + 2H_{ads} \rightleftharpoons YH{-}ZH_{ads} \tag{3}$$

$$YH{-}ZH_{ads} \rightleftharpoons YH{-}ZH \tag{4}$$

$$2H_{ads} \rightleftharpoons H_2 \text{ (Tafel step)} \tag{5a}$$

or

$$H_{ads} + H_3O^+(H_2O) + e^- \rightleftharpoons H_2 + H_2O \text{ (Heyrovsky step)} \tag{5b}$$

However the competition between the substrate hydrogenation and the hydrogen evolution reaction (HER) (Tafel 5(a) or Heyrovsky (5b) reactions) can drastically lower the current efficiency (CE) or prevent the ECH of substrates that are difficult to hydrogenate.

The competition between HER and ECH depends on several factors [1]. Thus previous studies have shown that cationic surfactants can strongly enhance the extent and the efficiency of the ECH of unsaturated compounds [2, 3]. This results mainly from the incorporation of the organic substrate in a hydrophobic surfactant layer adsorbed on the cathode. The consequent increase of the local substrate concentration on the catalyst favors reaction with the adsorbed hydrogen [2, 3]. High yields and current efficiencies were obtained for the ECH at RaNi cathodes of carvone, limonene and *p*-menthene emulsified in aqueous solutions in the presence of low amounts of didodecyldimethylammonium bromide (DDAB), a non-micelle-forming surfactant that gives strong adsorptions at the interfaces [3]. In the same way we have recently reported that the ECH of phenol into cyclohexanol is significantly improved at pH 2 by low amounts of DDAB [4]. However, this results from an increase in the surface coverage by adsorbed hydrogen and not from the adsorption of the organic substrate, which remains very low in the whole range of DDAB concentration used [4]. Thus the behavior of phenol is markedly different from that of the other unsaturated compounds. The association of organic substrates with micelles and surfactant layers depends on their hydrophobicity, which increases with the number and the length of alkyl substituents [5, 6]. Therefore, compared with phenol itself, a better association with the surfactant-adsorbed layer can be expected in the case of alkyl-substituted phenols. Moreover, hydrogenation of alkylphenols gives alkyl-substituted cyclohexanones and cyclohexanols of industrial interest; e.g. the *cis*-isomers of 2- and 4-*tert*-butylcyclohexanols are used in the perfume and fragrance industry. In consequence, we have studied the ECH of 2,6-dimethylphenol and 2-*tert*-butylphenol in aqueous buffers. This paper reports the influence of DDAB on the efficiency of the hydrogenation reaction and on the distributions of products and isomers. The catalytic hydrogenation of alkyl-substituted phenols is more difficult and occurs more slowly than that of phenol itself [7, 8]. A similar observation was earlier done by Sasaki et al. for the electrolytic hydrogenation of *para*-substituted phenols [9]. Robin et al. have previously shown that an increase of temperature caused a strong increase of the CE of the ECH reaction [10]. Therefore the ECH of alkylphenols was performed at 65 °C.

2. Experimental details

2.1. *Reagents*

Commercially available compounds were used as received: 2,6-dimethylphenol (99%), 2,6-dimethylcyclohexanone (98%), 2,6-dimethylcyclohexanol (99%) and didodecyldimethylammonium bromide (DDAB) (99%) from Aldrich, 2-*tert*-butylphenol (99%), 2-*tert*-butylcyclohexanone (97%) and 2-*tert*-butylcyclohexanol (99%) from Acros. Ethanol and water were distilled before use. The aqueous buffers were prepared as described in the Handbook of Chemistry and Physics (pH 2: HCl 0.04 M, KCl 0.16 M) [11] or from a titrisol Merck (pH 9: H_3BO_3/NaOH/KCl).

2.2. *Working electrodes*

The RaNi cathodes were prepared as already described [10] by codeposition on a stainless steel grid (3 cm × 4 cm) of nickel and of particles of Raney nickel alloy in a plating bath (constant current: 400 mA, amount of electricity: 1400 C for each side of the electrode), followed by leaching the aluminum in 30% aqueous NaOH (70 °C, 7 h). The percentage of the deposited alloy varied between 60 and 70% (this corresponds to 0.6–0.9 g RaNi catalyst after leaching).

2.3. *Electrolysis*

Electrolysis was carried out at 65 °C in a two-compartment jacketed glass H-cell with a Nafion 417 (Aldrich) membrane (7 cm^2) using a Tacussel PRT-100 potentiostat coupled to a Tacussel IG-5 LN coulometer. The potential was measured using an Ag/AgCl saturated KCl reference electrode (from Metrohm) (+197 mV vs NHE). In the anodic compartment, the counter electrode, a platinum perforated cylinder (4 cm long and 3 cm in diameter), was immersed in 100 ml of an aqueous solution of sulfuric acid 0.5 mol dm^{-3} (experiments at pH 2) or 0.05 mol dm^{-3} (experiments at pH 9). The cathodic electrolytes consisted of 100 ml of aqueous buffers (pH 2 or 9) with or without surfactant. The pH was controlled during electrolysis with Merk non-bleeding pH indicator strips [12].

In all solutions (with and without DDAB), at the concentration used (2×10^{-2} mol dm^{-3}), 2,6-dimethylphenol was entirely soluble and gave homogeneous solutions, whereas the low solubility of 2-*tert*-butylphenol led to the formation of emulsions (solubility values close to 5.7×10^{-3} (pH 2) and 6.7×10^{-3} (pH 9) mol dm^{-3} were estimated from UV absorbance measurements).

The electrolyses were conducted at low current densities (1.7 mA cm^{-2}) as previously described for the ECH of phenol [4]. In all experiments the theoretical amount of electricity (6 F mol^{-1} of phenol) was consumed. The progress of the electrolysis was followed by gas–liquid chromatography (GLC) on a Varian 3300 chromatograph equipped with a FID detector and a C-R 6A Shimadzu integrator, using a DB-Wax fused silica capillary column (from J & W Scientific) (30 m, 0.5 μm). Aliquots (0.5 ml) from the catholyte were extracted with ether after addition of 1 ml of saturated NaCl solution and acidification (pH $\simeq$ 1) with HCl. The products were identified by comparing their retention times with those of authentic samples (temperature programmes: 2,6-dimethylphenol: 70 –105 °C (5 °C min^{-1}) (2 min) –220 °C (10 °C min^{-1}); 2-*tert*-butylphenol: 50 °C (6 min) –120 °C (20 °C min^{-1}) (10 min) –195 °C (20 °C min^{-1}) (10 min)). The yields and the mass balance were determined by the internal standard method (internal standard: *n*-heptadecane or *n*-undecane (99%) Janssen Chemica).

2.4. *Products*

The cathodic aqueous solutions were saturated with NaCl, acidified (pH $\simeq$ 1) with HCl and extracted with ether. Quantitative analysis (yields and mass balance) was performed by GLC as indicated above. Then the ether was dried ($MgSO_4$), evaporated under vacuum and the mass balance was calculated from the weight of the crude product. In most experiments the crude product was also analyzed by ^1H NMR spectroscopy (on a Bruker AM 300 spectrometer). A good fit was observed for the data obtained with these different analyses.

2.5. *Studies of 2,6-dimethylphenol adsorption*

These studies were done with solutions and a cell identical to those used for the electrosynthesis. The amount of the substrate adsorbed on the cathode was estimated from the substrate concentration remaining in the bulk solutions. Aliquots (200 μl) were diluted in 10 ml aqueous buffer and the absorbance was recorded at 270 and 275 nm (on a Hewlett-Packard 8453 spectrophotometer).

3. Results and discussion

The hydrogenation of phenol and alkyl-substituted phenols can give different products depending on the catalyst (and its support) and the reaction conditions [13]. In our experimental conditions, in all media used, with and without DDAB, a mixture of 2-*tert*-butylcyclohexanone and 2-*tert*-butylcyclohexanol was obtained from the ECH of 2-*tert*-butylphenol. In contrast the ECH of 2,6-dimethylphenol led only to 2,6-dimethylcyclohexanol. Moreover, in all experiments, no side-products were detected.

As pointed out earlier for the hydrogenation of cresols [14], the formation of alkylcyclohexanols can involve two mechanisms: a direct route leading only to cyclohexanol without ketone (Figure 1, step 1) and a consecutive route which gives a mixture of the two products (Figure 1, steps 2 and 3) [8]. Among the different factors playing a part in the competition between these two pathways, the orientation of the aromatic ring could play a primary role as indicated by the previous investigations on phenol catalytic hydrogenation [15]. In their study of the gas-phase hydrogenation of phenol, Neri et al. have suggested that the reaction occurs between the activated hydrogen on the metal sites and the aromatic substrate chemisorbed on the support [15]. The formation of cyclohexanol (direct route) would be favored by a parallel orientation of the benzene ring and the surface of the catalyst [15]. In contrast a non-parallel orientation favors the stepwise addition of hydrogen (Figure 1, steps 2 and 3) leading to the formation of the intermediate cyclohexanone [15]. The adsorption mode depends on the acid-base properties of the catalyst. Taylor and Lundlum have shown that, on γ-Al_2O_3, the phenol and the methyl-substituted phenols molecules (anchored to the surface through the oxygen atom) are oriented with the aromatic ring 'co-planar' with the surface [16]. The presence of alumina formed during the lixiviation was previously demonstrated in the Raney nickel catalyst [17] and also on RaNi cathodes [18]. This could favour adsorption of the symmetrical substituted 2,6-dimethylphenol with the aromatic ring 'co-planar' with the surface of the Raney nickel catalyst. Therefore, in our experiments, the ECH of 2,6-dimethylphenol would occur by the direct route (Figure 1, step 1) leading to the formation of 2,6-dimethylcyclohexanol as sole product. With the 2-*tert*-butylphenol, in agreement with earlier studies [7], the presence of the bulky *t*-butyl group in the *ortho*-position favors the ketone formation. This could result from a steric hindrance effect which prevents a 'co-planar' orientation of the aromatic ring with the catalyst surface and therefore leads to a partial hydrogenation giving the 2-*tert*-butylcyclohexanone in a first step (Figure 1, step 2).

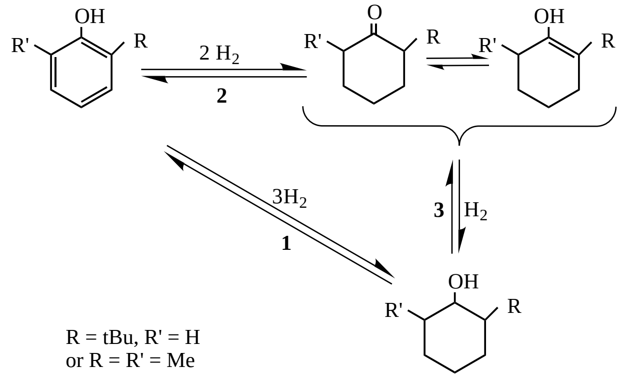


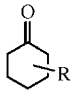
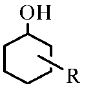
Fig. 1. Reaction scheme of alkylphenol hydrogenation.

3.1. *ECH in the absence of surfactants*

Several main points can be drawn from the results recorded in Table 1.

- A poor hydrogenation reaction (CE < 1 and 6%) was observed with the two substrates at pH 2 (entries 1 and 3). The ECH of 2,6-dimethylphenol and

Table 1. ECH of phenol and alkylphenols (2×10^{-2} mol dm^{-3}) at 65 °C, in aqueous buffers, on RaNi. Experimental conditions: constant current densities: 1.7 mA cm^{-2}, cathodic potential: −0.6 to −1 V vs Ag/AgCl, $Q = 6$ F mol^{-1}

Entry	Substrate	pH (initial–final)	Recovered substrate[a] /%	Yield[a] /%		Current efficiency[a] /%	Material balance[a] /%
							
1	2,6-dimethylphenol	2–3	91	0	0.13	0.13	92
2		9–10	74	0	8.5	8.5	83
3	2-*tert*-butylphenol	2–3	82	7	1	6	90
4		9–10.5	48	37	2.5	27	88
5	Phenol	2–3	63	0	33	33	96
6		9–10	3	0	89	89	92

[a] Determined by GLC and ^1H NMR.

2-*tert*-butylphenol was more efficient at pH 9 (CE 8.5 and 27%) (entries 2 and 4). As emphasised for the phenol and *p*-cresol hydrogenation [4, 19, 20], this influence of alkaline buffer could result from a higher rate of hydrogenation of the phenolate anions with respect to the phenols.

- Hydrogenation of 2,6-dimethylphenol is much less efficient than that of 2-*tert*-butylphenol. At pH 2 and 9, the CE of the ECH reaction is respectively 46-times and 3-times lower with the first substrate than with the second one. Moreover, both at pH 2 and 9, the current efficiencies observed with these two alkylphenols are much lower than those obtained at 65 °C for the ECH of phenol, namely 33 and 89% in acidic and alkaline solutions (entries 5 and 6). The hydrogenation rates of several alkylphenols on Ni and Pd/Al_2O_3 were recently measured by Tobiěik and Červeny [8]. In agreement with earlier results [7], the alkylphenol hydrogenation rate decreases with the number of alkyl-substituents and their bulkiness and with the increasing steric hindrance of the hydroxyl group [8]. As a consequence, the low efficiency of the ECH of 2,6-dimethylphenol and 2-*tert*-butylphenol, compared to that of phenol under the same experimental conditions, can be attributed to low hydrogenation rates in particular in the case of the di-substituted alkylphenol. In these conditions the HER (Reactions 5(a) and (b)) becomes the major process.
- In alkaline and acidic solutions the ketone is the major product of the ECH of 2-*tert*-butylphenol (respectively 94 and 88% of the mixture). So the consecutive route (Figure 1, steps 2 and 3) is largely predominant, if not the sole pathway.
- Two and three isomeric alkylcyclohexanols, respectively, are formed in the ECH of 2-*tert*-butylphenol and 2,6-dimethylphenol. This point will be studied in the next section with the results obtained in the presence of DDAB.

3.2. *ECH in the presence of didodecyldimethylammonium bromide (DDAB)*

Surfactants are widely used in electrochemistry both for analytical purposes and in electrosyntheses. The formation of microheterogeneous systems (micelles, microemulsions) and the adsorption of surfactants at the interfaces are two main features that can strongly influence an electrochemical process. Two parameters play fundamental roles in electrosyntheses; namely the solubilization equilibrium between the aqueous electrolyte and the micellar or the microemulsified pseudophase and the modification of the electrode by an adsorbed surfactant layer [21]. The latter is important with surfactants possessing two hydrophobic tails like DDAB, which gives strong adsorptions at the interfaces even at very low concentrations. All these points are developed in recent reviews [21–27].

3.2.1. *ECH of 2,6-dimethylphenol*

The current efficiencies (and the yields) and the isomer distributions obtained for the ECH of 2,6-dimethylphenol at pH 2 and 9 without surfactant and in the presence of increasing amounts of DDAB are recorded in Table 2.

The following main points can be drawn from these values obtained after the consumption of the theoretical amount of electricity (6 F mol^{-1}):

(i) In acidic solution the effect of DDAB on the extent and the efficiency of the ECH reaction is negligible as shown by the very slight difference of the CE values (0.13 and 2.5) (Table 2, entries 1 and 2) obtained when surfactant concentration increases from 0 to 5.4×10^{-5} mol dm^{-3}. With higher DDAB amounts, no hydrogenation occurs and the 2,6-dimethylphenol is quantitatively recovered.

(ii) In alkaline solution as the DDAB concentration increases from 0 to 2.16×10^{-3} mol dm^{-3} (Table 2,

Table 2. ECH of 2,6-dimethylphenol (2×10^{-2} mol dm^{-3}) in aqueous buffers, at 65 °C, on RaNi, pH 2 (entries 1, 2) and 9 (entries 3–9): influence of DDAB concentration
Electrolysis conditions: see Table 1.

Entry	[DDAB] /mol dm^{-3}	Unreacted 2,6-dimethylphenol[a] /%	Isomeric distributions[a,b]			Current efficiency and overall yield[a,c] /%	Material balance[a] /%
			1 /%	*2* /%	*3* /%		
1	0	91	70	0	30	0.13	92
2	5.4×10^{-5}	92.5	54	18	28	2.5	95
3	0	74	43	18	39	8.5	83
4	1.08×10^{-4}	87	47	15	38	8	95
5	2.16×10^{-4}	61	39	20	41	26	87
6	4.32×10^{-4}	56	35	22	43	30	86
7	1.08×10^{-3}	38	30	30	40	36	80
8	2.16×10^{-3}	14.5	32	35	33	70	84.5
9	4.32×10^{-3}	14	23	39	38	60	74

[a] Determined by GLC and ^1H NMR.

[b] Relative percentages.

[c] 2,6-dimethylcyclohexanol was the sole product and the theoretical amount of electricity was used, thus the overall yields of the three isomeric alcohols and the current efficiencies have the same numerical values.

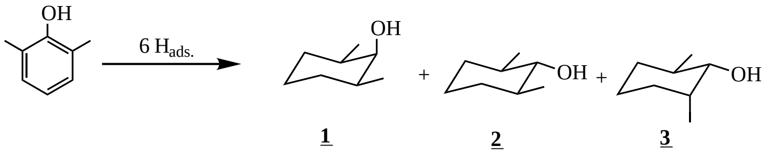


Fig. 2. Reaction scheme of ECH of 2,6-dimethylphenol.

entries 3–8) the CE rises from 8 to 70%. For a higher surfactant concentration a colloidal solution is formed and a slight decrease of the efficiency of the hydrogenation reaction is observed (CE $= 60\%$) (entry 9).

(iii) The ECH of 2,6-dimethylphenol gives three isomeric 2,6-dimethylcyclohexanols (Figure 2). The isomeric distribution depends on the pH as shown by the relative percentages observed in the experiments carried out without surfactant (Table 2, entries 1 and 3). At pH 2 (entry 1) isomer *1* was largely predominant (70%) and the more stable isomer *2* was not detected. Changing the acidic medium to an alkaline one (entry 3) led to a decrease in the relative percentage of *1* whose value at pH 9 was close to that of isomer *3* (respectively 43 and 39%) and an increase in the relative percentage of *2* (18%). The isomeric distribution is strongly modified at pH 9 by the presence of DDAB. In the whole range of surfactant concentration used, the relative percentage of isomer *3* is roughly constant and close to 40%. In contrast, the rise in amount of surfactant improves the formation of the most stable isomer *2* at the expense of isomer *1*, as shown by the variation in the relative percentages: 15–39% for *2* and 47–23% for 1 (Table 2, entries 4–9). At pH 2, a similar trend may occur, as indicated by the percentages of *1* and *2* obtained in the two experiments with and without DDAB (entries 1, 2).

The variation of the isomeric distribution with the pH is in agreement with earlier results [7, 28]: axial (*cis*) alcohols are the main hydrogenation products in acidic media (e.g. isomer *1*) and equatorial (*trans*) alcohols can be expected under neutral or alkaline conditions (e.g. isomers *2* and *3*). The increase in the formation of isomer *2* with increasing amounts of DDAB may result from an increasing adsorption (see below). This would favour isomerisation through a sequential dehydrogenation–hydrogenation process leading to the most stable isomer.

The strong catalytic effect observed at pH 9 and its absence at pH 2 can be rationalized as follows.

The hydrogen evolution and the ECH reaction were previously studied by Lasia and co-workers [1, 29, 30]. The rate of the hydrogenation reaction is given as $v = k^a\ \Theta_{sub}\ (\Theta_H)^x$ where k^a is the surface rate constant, x the reaction order with respect to the adsorbed hydrogen and Θ_{sub} and Θ_H the surface coverage by the adsorbed organic substrate and the adsorbed hydrogen, respectively [1]. In the study of the ECH of phenol [4] an increase in the Θ_H values in the presence of DDAB was found only in acidic medium. In alkaline medium the influence on Θ_H was negligible [4]. Thus the strong catalytic effect observed at pH 9 cannot result from a variation of Θ_H. The second parameter Θ_{sub} depends on the adsorption of 2,6-dimethylphenol, which was estimated from measurement of the alkylphenol concentration in the bulk solution (see Section 2.5). The percentage of adsorbed substrate is recorded in Figure 3 as a function of DDAB concentration.

No significant effect is observed at pH 2: the alkylphenol adsorption remains constant and close to 15% whatever the DDAB concentration is (Figure 3, curve 1). The very poor hydrogenation indicates that this adsorption value (higher than that previously observed with phenol itself [4]) is not enough to overcome a too low hydrogenation rate (i.e. the k^a value).

In contrast, in basic solutions, the percentage of adsorbed 2,6-dimethylphenol rises from 7% to a value close to 40%, as the amount of surfactant increases from 0 to 10^{-3} mol dm^{-3}. Beyond this concentration the adsorption remains roughly constant (Figure 3, curve 2). The improvement of the substrate adsorption at pH 9 may result from the electrostatic interaction between the cationic DDAB head groups and the phenate anions, which occurs only in basic solutions. Therefore, the significant increase of the efficiency of the ECH reaction obtained in alkaline solutions can be attributed, at least partially, to this growth of the substrate adsorption. As previously observed for the ECH of carvone and limonene [3], the maximum improvement of the hydrogenation is obtained for the surfactant concentration leading to the highest adsorption. This value, close to 2×10^{-3} mol dm^{-3}, is 10 times lower than that of the substrate. But it is significantly higher than the DDAB concentration (2.7×10^{-4} mol dm^{-3}) giving the best yield for the ECH of limonene [3]. This difference can be correlated to a large difference in adsorption: in the presence of 2.7×10^{-4} mol dm^{-3} of DDAB the most of the limonene was adsorbed on the cathode [3] whereas less than 20% of 2,6-dimethylphenol is adsorbed at the interface.

3.2.2. *ECH of 2-tert-butylphenol*

The results obtained after the consumption of the theoretical amount of electricity (6 F mol^{-1}) are reported in Tables 3 (pH 2) and 4 (pH 9). In all media the ECH of 2-*tert*-butylphenol gives 2-*tert*-butylcyclohexanone and 2-tert-butylcyclohexanol (Figure 4). The DDAB influence on the efficiency and the selectivity of the ECH are two main points that must be considered.

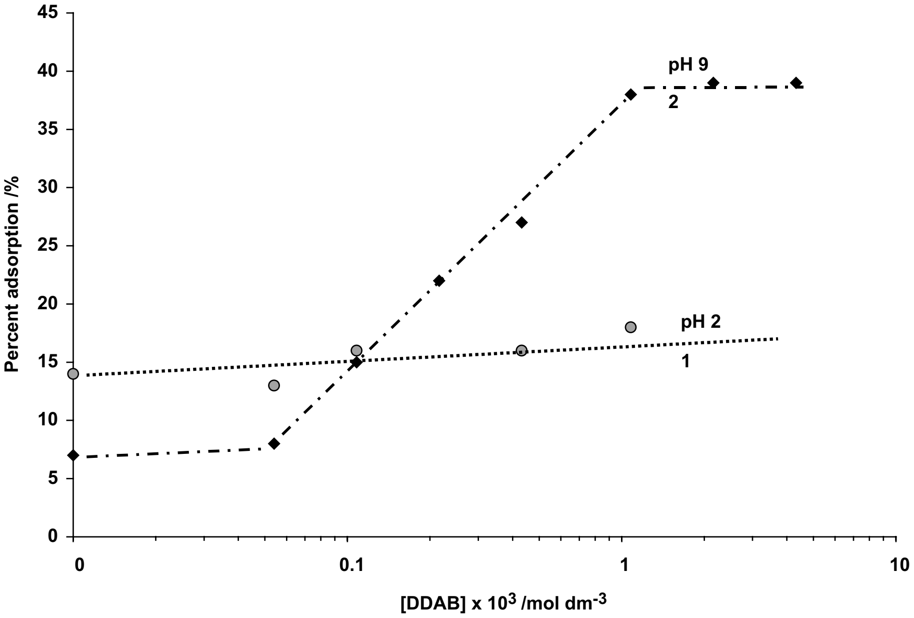
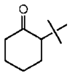
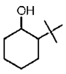


Fig. 3. Percentage of 2,6-dimethylphenol adsorbed at the interfaces as a function of DDAB concentration, pH 2 (curve 1) and pH 9 (curve 2).

Table 3. ECH of 2-*tert*-butylphenol (2×10^{-2} mol dm^{-3}) at 65 °C, pH 2[a], on RaNi: influence of DDAB concentration
Electrolysis conditions: see Table 1.

Entry	[DDAB] / mol dm^{-3}	Recovered 2-*tert*-butylphenol[b] /%	Yield[b] /%		Current efficiency[b] /%	Material balance[b] /%
				 ◆		
1	0	82	7	1	6	90
2	5.4×10^{-5}	69	20	3	16	92
3	1.08×10^{-4}	58	34	5[c]	28	97
4	2.16×10^{-4}	63	21	3	17	91
5	4.32×10^{-4}	62	17	9	20	87
6	1.08×10^{-3}	84	14	1.5	11	90
7	2.16×10^{-3}	70	10	10	17	90

[a] Initial and final values: 2 and 3; buffer: HCl 0.04 M, KCl 0.16 M [11].

[b] Determined by GLC and ^{1}H NMR.

[c] Diastereoisomeric *cis*/*trans* ratio: 96/4.

◆ The *cis*-isomer was the sole isomer detected by GLC except in entry 3.

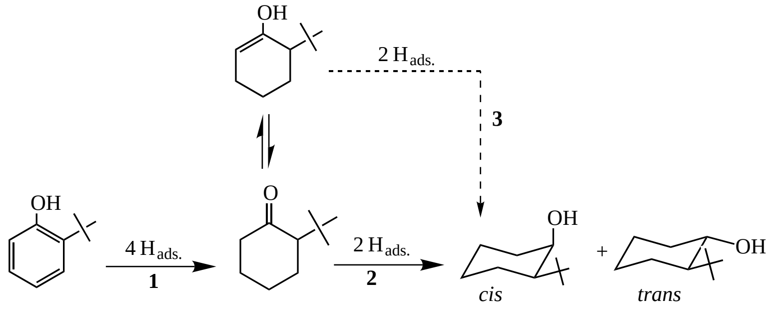
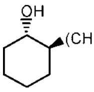
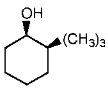
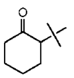
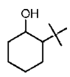


Fig. 4. Reaction scheme of ECH of 2-*tert*-butylphenol.

3.2.2.1. *Influence of DDAB on the hydrogenation efficiency.* In acidic and alkaline solutions, the efficiency of the ECH significantly increases with addition of low amounts of DDAB: the CE increases from 6% (pH 2) and 27% (pH 9), in the absence of surfactant, to 16–28% (pH 2) and 58–62% (pH 9) in the presence of DDAB concentrations ranging from 5×10^{-5} to 2×10^{-4} mol dm^{-3} (Table 3, entries 1–3 and Table 4,

Table 4. ECH of 2-*tert*-butylphenol (2×10^{-2} mol dm^{-3}) at 65 °C, pH 9[a], on RaNi: influence of DDAB concentration
Electrolysis conditions: see Table 1.

Entry	[DDAB]/ mol dm^{-3}	Recovered 2-*tert*-butylphenol[b] /%	Yield[b] /%		 *cis* /%[b,c,d]	 *trans* /%[b,c]	Current efficiency[b] /%	Material balance[b] /%
								
1	0	48	37	3	◆	◆	27	88
2	5.4×10^{-5}	20	31	37	92	8	58	88
3	1.08×10^{-4}	23	24	43	94	6	59	90
4	2.16×10^{-4}	18	23	47	95	5	62	88
5	4.32×10^{-4}	34	19	37	95	5	49	90
6	1.08×10^{-3}	29	20	43	95	5	56	92
7	2.16×10^{-3}	26	11	44	93	7	51	81

[a] Initial and final values: 9 and 10; buffer: H_3BO_3/NaOH/KCl (Titrisol Merck).
[b] Determined by GLC and ^{1}H NMR.
[c] Relative percentages.
[d] The relative percentage of the *cis*-isomer corresponds also to S_{cis}.
◆ The *cis*-isomer only was detected by GLC.

entries 1–4). For higher surfactant concentrations, considering the experimental uncertainties, the CE remains practically constant and close to 20% at pH 2 and 50% at pH 9 (Table 3, entries 4–7 and Table 4, entries 5–7). As with 2,6-dimethylphenol, this catalytic effect could result from an increase in the adsorption of 2-*tert*-butylphenol due to its hydrophobicity. However, the presence of an emulsion does not allow measurement of the adsorption phenomena in our experimental conditions. Indeed, during the major part of the electrolysis, the substrate concentration in the aqueous phase (estimated from UV absorbance measurement) remains constant and close to the saturation concentration.

The maximum CE value is twice as low at pH 2 (28%) (Table 3, entry 3) as at pH 9 (62%) (Table 4, entry 4). Once again, this can result from a higher rate of the hydrogenation of the phenolate anion with respect to the phenol [4, 19, 20].

Moreover in acidic solutions the CE improvement results essentially from the formation of 2-*tert*-butylcyclohexanone: its yield grows from 7 to 34% respectively without and with DDAB (Figure 5, curve 4 and Table 3, entries 1–3) whereas the yields of 2-*tert*-butylcyclohexanol remains low (⩽10%) whatever the DDAB concentration is (Figure 5, curve 1 and Table 3). In contrast, in alkaline solutions, the increase in the ECH efficiency due to the surfactant is related to a rise in

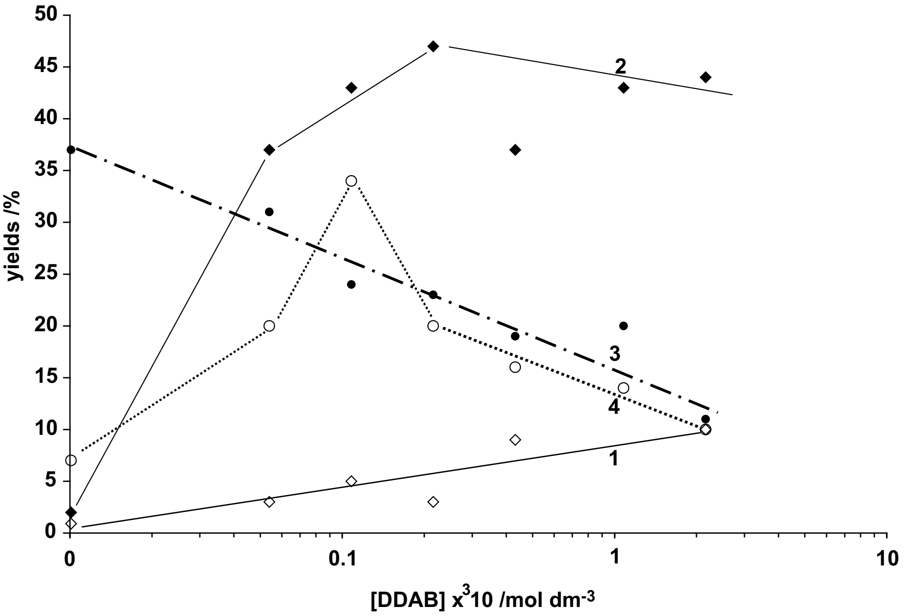


Fig. 5. Yields of products formed by ECH of 2-*tert*-butylphenol as a function of DDAB concentration. Key: 2-*tert*-butylcyclohexanol: (◇) pH 2 (curve 1) and (◆) pH 9 (curve 2); 2-*tert*-butylcyclohexanone: (○) pH 2 (curve 4) and (●) pH 9 (curve 3).

efficiency of the formation of 2-*tert*-butylcyclohexanol whose yield is strongly improved (from 3 to 47%) (Table 4, entries 1–4) as the amount of surfactant rises (Figure 5, curve 2). At the same time, the yield of 2-*tert*-butylcyclohexanone decreases from 37% (in the absence of DDAB) (Table 4, entry 1) to 11% (with the highest amount of DDAB) (Table 4, entry 7) (Figure 5, curve 3). The continuous lowering of 2-*tert*-butylcyclohexanone, as the yield of 2-*tert*-butylcyclohexanol rises, indicates that the latter compound is mainly formed at the expense of the former one. This observation and the large predominance of 2-*tert*-butylcyclohexanone at pH 2 suggest that, in all media (with and without DDAB), the consecutive route (Figure 1, steps 2, 3 and Figure 4, steps 1, 2, 3) represents the main, if not the sole, pathway.

3.2.2.2. *Influence of DDAB on the reaction selectivity*
Two types of selectivity represent important parameters in the ECH of 2-*tert*-butylphenol, namely the selectivity of the ketone formation S_k and the selectivity with respect to the ratio of *cis*/*trans*-2-*tert*-butylcyclohexanol S_{cis}:

$$S_k = [\text{ketone/ketone} + \text{alcohol}] \times 100$$

and S_{cis}=[*cis*-isomer/*cis*-isomer + *trans*-isomer] × 100.

Selectivity of ketone formation: S_k values close to 90% are obtained in experiments in which the conversion rates are lower than 50%, i.e. the first four experiments at pH 2 (Table 3, entries 1–4) and the one at pH 9 without DDAB (Table 4, entry 1). These values are in agreement with those (93%) found by Tobičik and Červeny for the catalytic hydrogenation of 2-*tert*-butylphenol over Ni/Al_2O_3 [8]. At pH 9, with increasing amounts of DDAB, a sharp decrease of S_k is observed (Figure 6, curve 1) and, at the same time, the conversion rate increases to a high value, i.e. 82% (corresponding to the minimum value of 18% for the recovered substrate) (Table 4, entry 4). This behaviour is similar to that observed by Kut et al. in their kinetic study of the catalytic hydrogenation of 2-*tert*-butylphenol over different catalysts (cf. the time-conversion diagram obtained with a Ni catalyst and recorded in Figure 6, Ref. [28]). The DDAB influence on S_k is much less pronounced at pH 2 (Figure 6, curve 2). This can be attributed to a low conversion rate, which never exceeds 42% (corresponding to 58% of recovered substrate) (Table 3, entry 3).

However, numerous literature results indicate that, on RaNi cathodes, the ECH of ketones into the corresponding alcohols is easy [1]. Cyclohexanone was quantitatively converted to cyclohexanol at RaNi cathodes in neutral and alkaline hydro-organic solutions with high CE (92–100%) [31]. In micellar and emulsified systems, the ECH at RaNi of carvone and of the intermediary formed dihydrocarvone and carvomenthone gave the corresponding alcohols with good yields and CE [2, 3]. Moreover Senda et al. have studied the ECH of 4-*tert*-butylcyclohexanone over different catalytic powder electrodes [32]. In the best conditions, over Raney Ni, 4-*tert*-butylcyclohexanol was formed with a good yield (82%) and a CE close to 35% (estimated from the yield and the amount of electricity used) [32]. In our experiments, the CE values for the conversion of 2-*tert*-butylcyclohexanone into 2-*tert*-butylcyclohexanol can be estimated assuming a material balance of 100%. Upper limits of 7 and 23% are found for the experiments carried out respectively at pH 2 and 9. In order to elucidate the poor efficiency of the 2-*tert*-butylcyclohexanone hydrogenation, the ECH of this compound

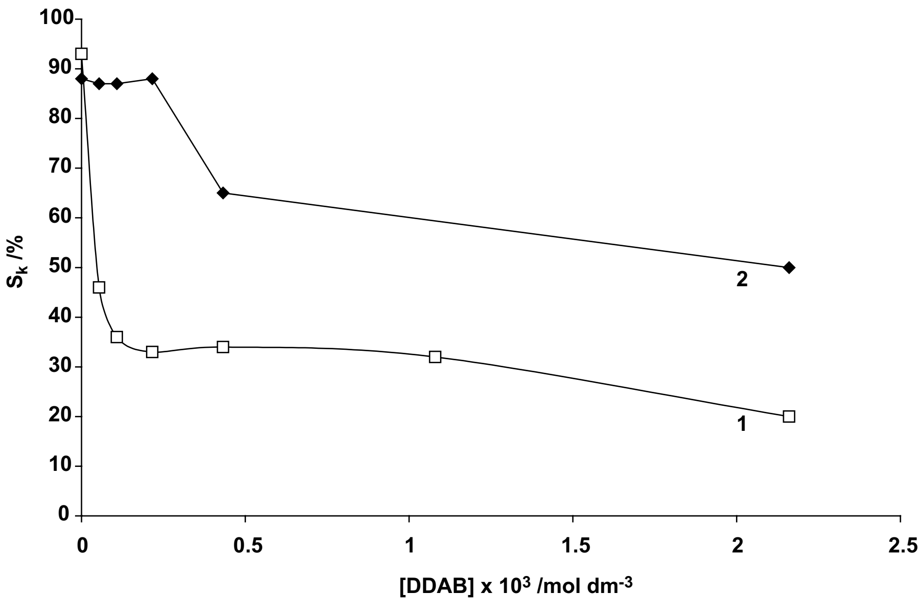
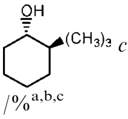
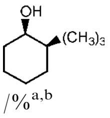


Fig. 6. Selectivity of the 2-*tert*-butylcyclohexanone formation (S_k) as a function of DDAB concentration (S_k = [ketone/ketone + alcohol] × 100). Key: (□) pH 9 (curve 1) and (♦) pH 2 (curve 2).

Table 5. ECH of 2-*tert*-butylcyclohexanone (2×10^{-2} mol dm^{-3}) at 65 °C, on RaNi, in aqueous buffers in the presence of DDAB (2.16×10^{-4} mol dm^{-3}). $Q = 2$ F mol^{-1}, other experimental conditions: see Table 1

Entry	pH (initial–final)	Recovered 2-*tert*-butylcyclohexanone[a] /%	 *cis* /%[a,b,c]	 *trans* /%[a,b]	CE and yield[a,d] /%	Material balance[a] /%
1	2–3	56	90	10	17	74
2	9–10	33	92	8	38	72

[a] Determined by GLC and ^{1}H NMR.

[b] Relatives percentages.

[c] The relative percentage of the *cis*-isomer corresponds also to S_{cis}.

[d] 2-*tert*-butylcyclohexanol was the sole product and the theoretical amount of electricity was used, thus yields and current afficiencies have the same numerical values.

was performed at 65 °C at pH 2 and 9 with a DDAB concentration (2.16×10^{-4} mol dm^{-3}) leading to the highest efficiency. After the consumption of the theoretical amount of electricity (2 F mol^{-1}) 2-*tert*-butylcyclohexanol was obtained with 17% (pH 2) and 38% (pH 9) yields and CE (Table 5). These results are in the same range as those observed for the 4-*tert*-butylcyclohexanone ECH [32], but they are lower than that obtained with the above-mentioned cyclohexanones. This can be attributed to the bulky *t*-butyl group in the *ortho*-position. Indeed, as mentioned in the literature [8], the steric hindrance of the carbonyl group slows down its hydrogenation rate. However, the comparison between the CE values observed for the formation of 2-*tert*-butylcyclohexanol by ECH of 2-*tert*-butylcyclohexanone (17 and 38%) and those estimated for the same conversion in the different ECH of 2-*tert*-butylphenol (<7 and <23%) suggests that the high relative percentages of the ketone in our experiments cannot result only from the slowdown of its hydrogenation rate. The poor formation of alcohol results also from the competition between the adsorption of the alkylphenol and that of the ketone. The adsorption of 2-*tert*-butylcyclohexanone can be reduced by the presence of an emulsified system. Indeed, due to its low solubility, a great part of the 2-*tert*-butylphenol remains emulsified during the electrolysis. This organic dispersed phase can extract the 2-*tert*-butylcyclohexanone and thus prevents its further hydrogenation. Several examples of product protection against further electrochemical conversion by their extraction into an organic dispersed phase are reported in the literature [21].

Cis-isomer selectivity: Both in acidic and basic solutions, the *cis*-isomer of the 2-*tert*-butylcyclohexanol is largely predominant. At pH 2 (Table 3), and pH 9 without DDAB (Table 4, entry 1), owing to the very low amounts of alcohol, only the *cis*-isomer can be detected by GLC. At pH 9 the *cis*/*trans* isomeric distribution remains constant and independent on the amount of DDAB. In the whole range of surfactant concentration used the S_{cis} values (corresponding to the relative percentage of the *cis*-isomer) lie between 92 and 95% (Table 4, entries 2–7). Similar values have been previously published for the catalytic hydrogenation of 2-*tert*-butylphenol: 92.5% [7], 81.9% [8]. In agreement with literature results [33], *cis*- and *trans*-2-*tert*-butylcyclohexanol are formed with the same selectivity ($S_{\text{cis}} = 90$–92%) (Table 5) by ECH of the 2-*tert*-butylcyclohexanone. All these results are consistent with a stepwise mechanism (consecutive path) for the ECH of 2-*tert*-butylphenol leading to 2-*tert*-butylcyclohexanone in a first step (Figures 1 and 4). The hydrogenation of the adsorbed carbonyl group of the ketone (Figure 4, step 2) leads to an alcohol with the hydroxyl group in the axial position (i.e. the *cis*-compound) as emphasized by several authors [33, 34]. Moreover, in agreement with earlier studies [8, 34] the enol form (2-*tert*-butylcyclohex-1-en-1-ol) of the ketone would be hydrogenated (Figure 4, step 3) to the *cis*-isomer.

4. Conclusions

The very poor yields and current efficiencies observed for the ECH of 2,6-dimethylphenol and 2-*tert*-butylphenol in aqueous buffers at Raney nickel cathodes are significantly improved in alkaline solutions by the presence of low concentrations of DDAB. This catalytic effect results mainly from an increase in the adsorption of the substrates due to their hydrophobicity. Thus the ECH of alkylphenols, at Raney Ni cathodes modified by the adsorption of small amounts of DDAB, represents a convenient method for the formation of alkylcyclohexanols. In particular the ECH of 2-*tert*-butylphenol leads, with a high diastereoselectivity, to *cis*-2-tert-butylcyclohexanol of industrial interest.

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