**ORIGINAL ARTICLE** 



# Cucurbit[5]uril-mediated electrochemical hydrogenation of $\alpha$ , $\beta$ -unsaturated ketones

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#### Abstract

The potential of cucurbit[5]uril to be used as inverse phase transfer catalyst in electrocatalytic hydrogenation of  $\alpha$ , $\beta$ unsaturated ketones is illustrated. The interaction behavior among isophorone and cucurbit[5]uril was also investigated using cyclic voltammetry and UV/vis absorption spectroscopy. The results concerning to both techniques revealed an enhancement in the intensity of the absorption peak and also in the current cathodic peak of isophorone in presence of cucurbit[5]uril. This achievement is related to the increase of the isophorone solubility in the medium being an indicative of a host-guest complex formation. The electrochemical hydrogenation of isophorone using cucurbit[5]uril was more efficient than others well-stablish methodologies. Regarding to (R)-(+)-pulegone and (S)-(+)-carvone, the use of cucurbit[5]uril leads to an increase of 17% and 9%, on average, respectively, in the yields when compared to the control reaction. The efficiency of selective C=O bond hydrogenation of 1-acetyl-1-cyclohexene was evaluated. The presence of cucurbit[5]uril increased by 12% the hydrogenations yields of 1-acetyl-1-cyclohexene when compared to the control reaction. In this sense, these results open up an opportunity to carry out electrocatalytic reactions within the cucurbit[5]uril environment.

Keywords Cucurbit[5]uril · Electrocatalytic hydrogenation · Inverse phase transfer catalyst · Isophorone · Voltammetry

# Introduction

It is well known that cavitands such as cyclodextrins [1-3], cucurbit[*n*]urils [4, 5], pyragallol[*n*]arenes [6], calix[*n*] arenes [7], cryptophanes [8, 9], can form a host-guest inclusion complex. One of the most popular examples of this kind of cavitands is the cyclodextrins. The chemistry of cyclodextrins has already been extensively reported [2, 3, 10–15]. Cyclodextrins are natural products composed of D-glucopyranosyl units having a toroidal shape with a hydrophilic exterior and lipophilic interior cavity (Fig. 1a and Table 1) [10, 16–19]. This amphiphilic character makes

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cyclodextrins water-soluble. The size of their nanometric hydrophobic cavity allows the formation of inclusion complexes with different hydrophobic substances [10].

Both cavities of the cyclodextrins differs in size and chemical nature, with the smaller cavity lined by primary hydroxyl groups and the larger one by secondary hydroxyl groups (Fig. 1a and Table 1). In this sense, through the host-guest, it is possible to enhance the solubility of hydrophobic molecules as well to improve and/or accelerate some organic reaction [2, 3, 15, 20–22].

The guest hydrophobicity plays also an important role in the stability of the host-guest complexes. Cucurbit[n]urils is not an exception of this rule. Cucurbit[n]urils belongs to a series of macromolecules ligands having an inner cavity and, therefore, with a potential host-guest binding capacity. Cucurbit[n]urils are pumpkin-shaped, highly symmetrical and rigid macromolecules, with negatively charged carbonyl rims and a lipophilic cavity (Fig. 1b) [4, 18, 23]. They are constructed of n-glycouril units bounded in rigid arrangement by methylene bridges. The number of glycouril units determines the portal size and the available volume of the cucurbit[n]urils (Table 1). They exhibit an equatorial

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Fig. 1 Structural comparison of cucurbit[n]urils and cyclodextrins: **a** D-glucopyranosyl units representation and general structure of cyclodextrins and **b** *n*-glycouril units and general representation of cucurbit[n]urils pumpkin-shape

Entry	Properties	Cyclode	extrins (CD	s)	Cucurbit[n]uril (CB[n])			
		αCD	βCD	γCD	CB[5]	CB[6]	CB[7]	CB[8]
1	Number of units	6	7	8	5	6	7	8
2	Molecular weigh (anhydrous)	972.85	1134.99	1297.14	830.7	996.84	1162.98	1329
3	Portal diameter (Å) <sup>a</sup>	4.7	6.0	7.5	2.4	3.9	5.4	6.9
4	Inner cavity diameter (Å) <sup>b</sup>	5.3	6.5	8.5	4.4	5.8	7.3	8.8
5	Cavity volume (Å <sup>3</sup> )	174	262	427	82	164	279	479
6	Cavity height (Å)	7.9	7.9	7,9	9.1	9.1	9.1	9.1

<sup>a</sup>Narrowed rim of CDs; <sup>b</sup>wider rim of CDs

symmetry plane, making both cavity openings identical (Fig. 1b). Their total depth is 9.1 Å but shown variations in cavity width among their different analogues (Table 1).

The first production of cucurbit[n]urils was reported by Behrend and coworkers in 1905 [24]. The authors reported the synthesis of a pumpkin-shaped molecule with six glycouril unit named as cucurbit[6]uril. In the early 2000 s cucurbit[n]urils with different sizes (n=5,7,8), namely respectively, cucurbit[5]uril, cucurbit[7]uril, cucurbit[8]uril have been synthesized by Kim et al. [25]. The potential of CB[n] catalyze chemical reactions starting from Mock work

**Table 1** Structural parametersand properties of cucurbit[n]urils and cyclodextrins [11,

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[26] on dipolar cycloadditions catalyzed by cucurbit[6]uril. Otherwise, cucurbit[7]uril has been employed to catalyze photolysis of bicyclic azoalkanes by transition metal ions coordinated to the cucurbit[7]uril rim [27]. Additionally, Barooah et al. [28] reported the manipulations of the photochemical reactivity of coumarin derivatives in presence of cucurbit[8]uril. Although cucurbit[5]uril shares similar binding properties with other members of the cucurbit[*n*] urils family, it small inner volume (Table 1) greatly limits its use in host-guest chemistry when compared to the larger homologues.

Accordingly to the green chemistry principles, a nontoxic, non-inflammable, abundantly available, inexpensive and of lower risk solvent to human health should be preferred in organic reactions [29]. In this sense, water should be the first choice among the chemists not only because it is environmentally acceptable but also due to the mechanistic point of view [30]. However, the most of substrates used in organic or electroorganic synthesis are insoluble in water leading to an overall yield drop of the reactions making it use limited. One approach described in the literature to overcome this limitation is the use of inverse phase transfer catalyst (IPTC) in which the low soluble substrate is transferred by the IPTC from the organic into the aqueous phase through the host-guest complexation.

The first use of IPTC agent has been reported by Zahalka et al. [31] and Harada and co-workers [32]. Baur et al. [33] reported the use of calix[*n*]arenes as IPTC in Suzuki coupling reaction of phenyl boronic acid and iodobenzene in aqueous solution. The authors show that the efficiency of the tested calix[*n*]arenes was higher than that for  $\beta$ -cyclodextrin. Mortreux and coworkers use modified  $\beta$ -cyclodextrin (per(2,6-di-*O*-methyl)- $\beta$ -cyclodextrin) as IPTC in rhodiumcatalyzed hydroformylation of a variety of water-insoluble terminal olefins achieving high yields and selectivity [20].

In the electrocatalysis field, Maiorova et al. [34] have applied β-cyclodextrin in the electrochemical hydrogenation (ECH) of acetophenone and methyl-4-isobutylacetophenone in both different solutions (water and water:ethanol) reaching high conversions (90%). Farnia et al. [35] studied the electrochemical reduction of acetophenones in aqueous alkaline solutions, in absence and presence of  $\beta$ -cyclodextrin, leading to D,L and meso pinacols (head-to-head dimers) as products. Amatore et al. [36] described the electrochemical behaviors of a variety of acetophenones in the presence of  $\alpha$ -,  $\beta$ -, and methyl- $\beta$ -cyclodextrin, in different solvents. The authors showed that, in dimethylformamide, cyclodextrin act as weak proton donors towards the electrogenerated acetophenone anion radical favoring the head-to-tail coupling. Vilar and Navarro [2] studied the ECH of benzaldehyde in water, using a nickel sacrificial anode (SA) (henceforward referred as ECHSA) and  $\beta$ -cyclodextrin as IPTC. The results showed that using  $\beta$ -cyclodextrin the yield of benzyl alcohol was 27% higher than that obtained in the absence of the IPTC. Thus, it should be possible to anticipate that other cavitands with similar dimensions and hydrophobicity inner properties can be used as IPTC. Even though cucurbit[5]uril is not big enough to accommodate large molecules into its cavity, its small size may be used to solve the mass-transport limitations in electrocatalytic reactions.

In this context, we describe the first use of cucurbit[5]uril in the ECHSA of  $\alpha$ , $\beta$ -unsaturated ketones in water using an undivided electrochemical cell. Isophorone (IUPAC name: 3,5,5-trimethyl-2-cyclohexen-1-one) was adopted as the standard substrate. Moreover, different organic substrates were tested, taking into account structural variations. Finally, this study is relevant from both electrocatalytic, supramolecular and green standpoint because there are no studies reporting the use cucurbit[5]uril as IPTC on the ECHSA methodology.

# Experimental

# Chemicals

Reagent-grade chemicals were used without further purification. Isophorone (97%), (R)-(+)-Pulegone (97%), 1-acetyl-1-cyclohexene (97%), 1-cyclohexyl-ethanol (97%) and (S)-(+)-carvone (96%) were purchase from Sigma Aldrich. Diethyl ether and ammonium chloride (supporting electrolyte) were purchased from Vetec and used as received. Sodium sulphate was purchased from Acros. Cucurbit[5] uril,  $\alpha$ - and  $\beta$ -cyclodextrin (Aldrich) were used as received. Deionised water, obtained by a Mili-Q system, was used as solvent in all experiments.

# Procedures

#### UV/vis spectroscopy

UV/vis spectrums were recorded (Cary 50 Probe) with a full-length range of 190–350 nm for aqueous solutions of the isophorone (6.1 mmol  $L^{-1}$ ) in absence and presence of different concentrations of cucurbit[5]uril, from 3.5 to 7.4 mmol  $L^{-1}$ . The resulting solutions were irradiated by ultrasound for 5 min and then added to a quartz cuvette with 1.0 cm optical path length and taken to record the spectrums.

#### **Electrochemical experiments**

The electrochemical experiments were run with a potentiostat/galvanostat Autolab PGSTAT101 (Eco Chemie, Utretch, The Netherlands) controlled by a personal computer running NOVA software (version 1.11.2).

#### Cyclic voltammetry

The cyclic voltammetry experiments were carried out at room temperature in a standard undivided three-electrode cell with a capacity of 10 mL. The working, reference and counter electrodes were a glassy carbon electrode ( $\phi = 3 \text{ mm}$ ), a home-made AglAgCllKCl (3 mol L<sup>-1</sup>) electrode [37] and a platinum coiled wire, respectively.

Electrochemical studies were performed by using a  $0.2 \text{ mol } \text{L}^{-1}$  of NH<sub>4</sub>Cl aqueous solution as supporting electrolyte. The glassy carbon working electrode was polished to

a mirror-like using an alumina suspension (0.3  $\mu$ m particle size) with a microcloth polishing pad before and between each cyclic voltammetry measurement. This procedure was performed to ensure the removal some possible adsorbed species. The potential range studied in cyclic voltammetry experiments started from 0 to -1.65 V at a scan rate of 100 mV s<sup>-1</sup>.

The presence of cucurbit[5]uril toward the electrochemical reduction of isophorone was evaluated. For this purpose, 10 mL of an aqueous solution of isophorone (2.6 mmol L<sup>-1</sup>) in 0.2 mol L<sup>-1</sup> NH<sub>4</sub>Cl was prepared. The resulting solution was stirred for 24 h and added to the electrochemical system. Different dispersions of cucurbit[5]uril ranging from 0.614 to 1.32 mmol L<sup>-1</sup> were prepared directly in 0.2 mol L<sup>-1</sup> of NH<sub>4</sub>Cl. The cyclic voltammetry experiments of the cucurbit[5]uril dispersions in presence of isophorone (2.6 mmol L<sup>-1</sup>) were conducted as mentioned before.

#### Electrochemical hydrogenation procedure

A nickel rod was used as sacrificial anode (0.1 dm diameter; 0.078 dm<sup>2</sup> area). Another Ni bar (0.1 dm diameter; 0.078 dm<sup>2</sup> area) was also used as the working electrode. Deionised water was used as solvent in all electrochemical hydrogenation experiments.

In order to evaluate both the cyclodextrin and cucurbit[5] uril influence on the electrocatalytic system, aqueous stock solutions of  $\alpha$ -cyclodextrin and  $\beta$ -cyclodextrin and cucurbit[5]uril were prepared. A 4.0 mL aliquot of the stock solution was mixed with 1.0 mmol of the substrate and stirred for 1 h. After that, the electrolytic cell containing both the working electrode (Ni) and the sacrificial anode (Ni), were filled with 6.0 mL of the supporting electrolyte (0.2 mol  $L^{-1}$ ). At this point, the final concentrations of species in solution were: 1.2 mmol  $L^{-1}$  of  $\alpha$ -cyclodextrin or  $\beta$ -cyclodextrin or cucurbit[5]uril. Electrolysis was carried out by using a gradient current density initially at 350 mA dm<sup>-2</sup>. After passage of the first half-charge (96.50 C or  $1.0 \text{ F mol}^{-1}$ ), the current density was decreased to 300 mA dm<sup>-2</sup> (passing the second half-charge; 48.25 C or 0.5 F mol<sup>-1</sup>), and successively to  $250 \text{ mA dm}^{-2}$  (third half-charge; 24.12 C or 0.25 F moL<sup>-1</sup>) and 200 mA dm<sup>-2</sup> (fourth half-charge; 12.06 C or 0.125 F  $mol^{-1}$ ).

After the electrolysis, the water solution was extracted with diethyl ether and dried with Na<sub>2</sub>SO<sub>4</sub>. Product analysis was performed primarily by gas chromatography with flame ionization (GC-FID) or mass spectral detection (GC-MS). GC-FID measurements were conducted on a Varian 3380 GC gas chromatograph equipped with a flame ionization detector. This GC-FID instrument was operated with a 30 m × 0.25 mm column, with a 0.25 µm dimethylpolysiloxane lining and a guard column. 2 µL sample was injected at a temperature of 250 °C in split mode with a 200:1 ratio. The temperature program started from 60 °C for 2 min followed by a 10 °C min<sup>-1</sup> ramp up to 220 °C, where this temperature was held for 2 min. For 1-acetyl-1-cyclohexene, comparisons with authentic samples were performed by GC in order to identify the hydrogenation products. Toluene (0.067 mmol) was used as an internal standard.

GC-MS measurements was conducted on a Shimadzu GC-MS model GC17A, a 70 eV ion trap, fitted with a 30 m capillary TGMS - 5 (HP) column. The temperature program started from 60 °C for 3 min followed by a 10 °C min<sup>-1</sup> ramp up to 240 °C and 60 °C min<sup>-1</sup> ramp up to 3000 °C, where this temperature was held for 4 min.

# **Results and discussion**

# UV/vis spectroscopy behavior of isophorone in presence of cucurbit[5]uril

UV/vis spectra of cucurbit[5]uril and isophorone were recorded at room temperature (Fig. 2a). Isophorone show an absorption band  $(\lambda_{max})$  at 240 nm which corresponds to the  $n \to \pi^*$  and  $\pi^* \to \pi^*$  transitions of the chromophores C=O and C=C, respectively of the  $\alpha$ , $\beta$ -unsaturated carbonyl system of isophorone [38, 39]. As can be notice in Fig. 2a, b and Table 2 (spectra 2–7), an enhancement in the absorption intensity of isophorone was observed due to the presence of cucurbit[5]uril. A hypsochromic shift of 1 nm was observed in presence of cucurbit[5]uril (3.50 mmol  $L^{-1}$  or 0.57 equivalents) into isophorone solution (Table 2, entry 2 and Fig. 2a) which persisted up to 7.40 mmol  $L^{-1}$  (1.21 equivalents) of cucurbit[5]uril. These findings and observation are an indicative of the host-guest inclusion formation due to the change of environment around the chromophore group of isophorone.

## Electrochemical behavior of isophorone in absence and presence of cucurbit[5]uril

The electrochemical reduction behavior of isophorone in absence and presence of cucurbit[5]uril was evaluated using cyclic voltammetry technique at glassy carbon electrode. Figure 3 displays the cyclic voltammograms of isophorone (2.6 mmol L<sup>-1</sup>) aqueous solution containing 0.2 mol L<sup>-1</sup> of NH<sub>4</sub>Cl, as supporting electrolyte, in absence and presence of increased amounts of cucurbit[5]uril, recorded on glassy carbon electrode at scan rate of 100 mV s<sup>-1</sup>.

It is possible to observe an irreversible reduction signal at -1.57 V vs. AglAgCllKCl (3 mol L<sup>-1</sup>). The signal around -0.65 V is related to the reduction of dissolved oxygen. From the data it is possible to observe an increase of the current of cathodic peak with the increase of the concentration of cucurbit[5]uril until 0.746 mmol L<sup>-1</sup>. Furthermore,

**Fig. 2** a Absorption spectra ( $\lambda$ = 240 nm) for 6.1 mmol L<sup>-1</sup> of isophorone with different equivalents of cucurbit[5]uril: (a) 0.0; (b) 0.57 (3.5 mmol  $L^{-1}$ ); (c)  $0.68 (4.2 \text{ mmol } \text{L}^{-1});$ (d) 0.80 (4.9 mmol  $L^{-1}$ ); (e) 1.01 (6.2 mmol  $L^{-1}$ ); (f) 1.08  $(6.6 \text{ mmol } L^{-1}) \text{ and } (g) 1.21$  $(7.4 \text{ mmol } L^{-1})$ . **b** Absorption spectra changes in the presence of different equivalents of cucurbit[5]uril: ((a)  $0.0 (\lambda = 242 \text{ nm});$  (b) 0.57 $(3.5 \text{ mmol } L^{-1}; \lambda = 241 \text{ nm});$ (c)  $0.68 (4.2 \text{ mmol } \text{L}^{-1};$  $\lambda = 241 \text{ nm}$ ; (d) 0.80 (4.9 mmol  $L^{-1}$ ;  $\lambda$ =241 nm); (e) 1.01 (6.2 mmol  $L^{-1}$ ;  $\lambda = 241 \text{ nm}$ ; (f) 1.08  $(6.6 \text{ mmol } \text{L}^{-1}; \lambda = 241 \text{ nm})$ and (g) 1.21 (7.4 mmol  $L^{-1}$ ;  $\lambda = 241 \text{ nm}$ 



**Table 2** UV-vis spectral data of 6.1 mmol  $L^{-1}$  isophorone in waterwith increasing concentration of cucurbit[5]uril at 298 K

Spectra	[CB[5]] (mmol L <sup>-1</sup> )	Absorbance (a.u.)	$\begin{array}{l}\lambda_{max}\left(nm\right)\\at\ 298\ K\end{array}$
1	0.00	2.36	242
2	3.50	2.45	241
3	4.20	2.46	241
4	4.90	2.48	241
5	6.20	2.51	241
6	6.60	2.54	241
7	7.40	2.56	241

the reduction potential of isophorone does not shift significantly in presence of cucurbit[5]uril at different dispersions concentrations when compared to the cyclic voltammogram of isophorone in absence of cucurbit[5]uril. Accordingly to Zuman and coauthors [40–42], for  $\alpha$ , $\beta$ -unsaturated ketones it was recognized that the products of their two-electron and two-proton reduction in aqueous media are saturated ketones. This reaction course was later confirmed for different  $\alpha$ , $\beta$ -unsaturated ketones [40, 41] and no exception was reported until now. In this sense, the results concerning to Fig. 3 may suggest that, in presence of cucurbit[5]uril, the redox center of isophorone could be located outside of the cavity. [43]. On the other hand, the current cathodic peak decreased in the higher cucurbit[5]uril dispersion concentration (1.32 mmol  $L^{-1}$ ). This behavior may be due to the fact that cucurbit[5]uril dispersed in solution could increase the isophorone solubility, therefore, a greater amount of



**Fig. 3** Cyclic voltammograms of isophorone [blue dashed line, (a) 2.6 mmol  $L^{-1}$ ] and 0.2 mol  $L^{-1}$  NH<sub>4</sub>Cl aqueous solution recorded at glassy carbon electrode at 100 mV s<sup>-1</sup>. In the presence of cucurbit[5] uril: (b) 0.614 mmol  $L^{-1}$ , (c) 0.746 mmol  $L^{-1}$  and (d) 1.32 mmol  $L^{-1}$ . (Color figure online)

molecules can reach the glassy carbon electrode surface. As expected, and corroborating the previously discussion concerning to UV-vis spectra (Fig. 2a, b), these preliminary observation open up an opportunity to perform electrocatalytic reactions within the confined cavity of cucurbit[5]uril.

### The cucurbit[5]uril effect on ECHSA of isophorone

Before discussing the cucurbit[5]uril influence in the ECHSA process, we would like to make some considerations

about general aspect of the ECH. According to Lessard [44], the ECH involves the generation of chemisorbed hydrogen, by reduction of water or hydronium ions (Eq. (1)). The next step is the reaction of the adsorbed organic substrate with the chemisorbed hydrogen (Eq. (5)), followed by the desorption of the hydrogenated product (Eq. (6)). In this sense, the efficiency of the ECH is directly proportional to the ratio of the catalytic hydrogenation rate (Eqs. (4)–(6)) over the hydrogen generation rate (Eqs. (2) and (3)).

$$H_3O^+ + e^- + M \rightarrow MH_{ads} + H_2O \tag{1}$$

$$2MH_{ads} \rightarrow M + H_2 \tag{2}$$

 $H_3O^+ + MH_{ads} + e^- \rightarrow M + H_2 + H_2O$ (3)

$$Y = Z + M \to M(Y = Z)_{ads}$$
<sup>(4)</sup>

 $2MH_{ads} + M(Y = Z)_{ads} \rightarrow M(YH - ZH)_{ads}$ (5)

$$M(YH - ZH)_{ads} \rightarrow M + YH - ZH$$
(6)

The ratio (hydrogenation/hydrogen generation) is affected by the unsaturated organic substrate. For a given unsaturated organic molecule, one of the factors which influence its adsorption is concentration and/or solubility. Therefore, any experimental alternative that results in the increase of the solubility of an unsaturated molecule, will favors the probability of reaction among both the adsorbed organic molecule and hydrogen and, as a consequence, raise the reaction yields.

Thus, the results concerning the ECHSA of isophorone in the presence of cucurbit[5]uril and cyclodextrins are summarized in Table 3. Isophorone is a  $\alpha$ , $\beta$ -unsaturated ketone widely used as solvent and it ECH proceeds given significant industrial products. The selective hydrogenation of the C=C bond in the organic chain of isophorone leads to dihydroisophorone (saturated ketone, SONE), an important

Table 3	Cucurbit[5]uril	effect on the	ECHSA	of isophorone
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pharmaceutical intermediate used as a solvent for vinyl resins [45], whereas a selective hydrogenation of the C=O bond leads to isophorol (unsaturated alcohol, UOL). It is know that conventional processes of isophorone hydrogenation produces a low overall conversion with a high selectivity to dihydroisophorone or a high overall conversion with poor selectivity for this product [45–48]. In this work, isophorone was selectively hydrogenated by ECHSA producing dihydroisophorone in good yields (Table 3, entries 2–4) after the passage of 2 F mol<sup>-1</sup>.

As can be seen, the use of cucurbit[5]uril furnish a slight gain of 8% (Table 3, entry 4), on average, in the hydrogenation yield when compared to the same reaction in the absence of the IPTC (Table 3, entry 1). Furthermore, the ECHSA in presence of cucurbit[5]uril was more efficient than that electrochemical systems using water:methanol (Table 3, entries 5 and 6) [49]. Indeed, accordingly to Pemberton et al. [43] in catalysis within confined environments the background reactivity outside the supramolecular reaction cavity must be lower than the reactivity inside of the supramolecular vessel. Thus, cucurbit[5]uril presents the ability of scavenger the isophorone into a confined environment increasing it solubility and, as a consequence, the probability of collision between both the isophorone and hydrogens adsorbed in the cathode matrix.

As expected, the use of the  $\beta$ -cyclodextrin or  $\alpha$ -cyclodextrin in the ECHSA leads to higher hydrogenation yields (68% and 59%, Table 3, entries 2 and 3, respectively), which represents an increase of 19.5% and 10.5% in the yields, respectively, when compared to that obtained in the absence of the IPTC (Table 1, entry 1). The better performance of both  $\alpha$ - and  $\beta$ -cyclodextrin over cucurbit[5]uril is related with the size of the cavity portal. Indeed, the smaller size of the portal and inner cavity diameter of the cucurbit[5]uril (2.4 and 4.4 Å, Table 1, entries 3 and 4) seems does not favor the complexation equilibrium, which is better

Entry	IPTC	Solvent	Cathode	Charge (F	[IPTC] <sub>final</sub>	Yield (%)	Products		Reference
				$mol^{-1}$ )	$(\text{mmol } L^{-1})$		SONE	SOL	
1	_a	H <sub>2</sub> O	Ni	2.0	_	$48.5 \pm 1.0$	48.5	0.0	This work
2	$\beta CD^b$	H <sub>2</sub> O	Ni	2.0	1.2	$68.0 \pm 1.5$	68.0	0.0	This work
3	$\alpha CD^{b}$	H <sub>2</sub> O	Ni	2.0	1.2	$59.0 \pm 1.0$	59.0	0.0	This work
4	CB[5] <sup>b</sup>	H <sub>2</sub> O	Ni	2.0	1.2	$56.5 \pm 1.0$	56.5	0.0	This work
5	_	H <sub>2</sub> O/MeOH	C/poly PPV <sup>2+</sup> -Pd <sup>c</sup>	2.0	-	13.0	13.0	0.0	[46]
6	-	H <sub>2</sub> O/MeOH	C/poly1.Ni(0)	2.0	-	33.0	27.0	6.0	[45]

<sup>a</sup>Control reaction, i.e. without using IPTC: 10.0 mL of NH<sub>4</sub>Cl solution (0.2 mol dm<sup>-3</sup>); isophorone (1 mmol); j = 350-250 mA dm<sup>-2</sup>; Ni cathode; Ni sacrificial anode; stirring. Reactions made in triplicate

<sup>b</sup>Electrolysis conditions: 10.0 mL of NH<sub>4</sub>Cl solution (0.2 mol dm<sup>-3</sup>); ISP (1 mmol); j = 350-250 mA dm<sup>-2</sup>; Ni cathode; Ni sacrificial anode; stirring. Reactions made in duplicate

<sup>c</sup>Poly(pyrrole-vio1ogen) film

supported by the larger portal and inner cavity diameter of  $\alpha$ -cyclodextrin (5.3 and 4.7 Å Table 1, entries 3 and 4) and  $\beta$ -cyclodextrin (6.5 and 6.0 Å, Table 1, entries 3 and 4). Based on the results and in the fact that catalysis within cucurbit[*n*]urils can occur at the rim (carbonyl portal) [43] it is reasonable to suggest that the ECHSA of isophorone may occur accordingly to the Scheme 1.

# ECHSA of $\alpha$ , $\beta$ -unsaturated ketones in presence of cucurbit[5]uril

Table 4 shows the comparison between different ECH procedures described in the literature and the ECHSA process described in this work for different  $\alpha$ , $\beta$ -unsaturated ketones.

(R)-(+)-Pulegone is an exocyclic unsaturated terpenone that can be hydrogenated, generating (-)-menthone,

Scheme 1 General cycle of isophorone ECHSA mediated by cucurbit[5]uril

(+)-isomenthone, (+)-neomenthol, (–)-menthol, (+)-neoisomenthol and (–)-isomenthol. In this work, (R)-(+)-pulegone was electrocatalytically hydrogenated by ECHSA in presence of cucurbit[5]uril and, after the consumption of 4 F mol L<sup>-1</sup>, only (–)-menthone and (+)-isomenthone (saturated ketones, SONE) were produced. The use of cucurbit[5] uril leads to an increase of 17% in the hydrogenation yield when compared to the control reaction (Table 4, entry 1).

The (S)-(+)-carvone, a conjugated cyclohexenone containing an exocyclic C=C bond can be also hydrogenated, producing dihydrocarvone, carvotanacetone and carvomenthone (saturated ketones, SONE), dihydrocarveol and carveol (unsaturated alcohols, UOL) and carvacrol (saturated alcohol, SOL). As expected, the conjugated endocyclic C=C bond was hydrogenated faster than the carbonyl group and dihydrocarvone was the main product in all experiments (Table 4,



Table 4	ECHSA of unsaturated keto	mes in presence of Cl	B[5]								
Entry	Substrate	Cathode	IPTC	Solvent	Charge	Products (%)			SOL + SONE	SOL + UOL	Ref.
						SONE	NOT	SOL	(%)	(%)	
-		Ż	اح	H <sub>2</sub> O	4.0	52.0 ± 1.0	0.0	0.0	52.0	0.0	This work
5	,O	Ni	$CB[5]^{a}$	$H_2O$	4.0	$69.0 \pm 1.0$	0.0	0.0	0.69	0.0	This work
ŝ		Ņ	٩	$H_2O$	4.0	48.0 ± 1.2	0.0	0.0	48.0	0.0	This work
	Ĭ										
4		Ni	$CB[5]^{a}$	$H_2O$	4.0	$57.0 \pm 1.0$	0.0	0.0	57.0	0.0	This work
5		C/poly1.Ni(0) <sup>e</sup>	I	H <sub>2</sub> O/MeOH	6.0	46.0	35.0	17.0	63.0	52.0	[48]
9		Raney Ni <sup>f</sup>	I	H <sub>2</sub> O/MeOH	6.0	16.0	0.0	44.0	60.0	44.0	[50]
7		Raney Ni <sup>f</sup>	I	Micellar <sup>c</sup>	6.0	25.0	0.0	62.0	87.0	62.0	[50]
8		Ni	٩	$H_2O$	4.0	$70.0 \pm 1.0$	0.0	3.0	73.0	3.0	This work
c		Ĩ	CDISI	0 n	01	20702	5 U + U S	20400		0.61	This more
10		p!N	[v]u)	H,O/MeOH	4.0	0.00 ± 0.00	0.0 ± 0.0	2.0 ± 0.0 2.0	92.0	2.0	11115 WOLD
11		Ni	I	2 Η <sub>2</sub> Ο/ΜεΟΗ	6.0	91	0.0	3.0	94.0	3.0	[54]
<sup>a</sup> Electro made ir <sup>b</sup> Contro triplicat	olysis conditions: 10.0 mL of 1 duplicate 1 reaction, i.e. without using te	f NH <sub>4</sub> Cl solution (0.2 IPTC: 10.0 mL of N <sup>1</sup>	2 mol dm <sup>-3</sup> ); H <sub>4</sub> Cl solution	1 mmol of substr 1 (0.2 mol dm <sup>-3</sup> );	ate; 1.2 mm 1 mmol of s	ol L <sup>-1</sup> of CB[5] ubstrate; $j = 35$	j; j = 350-250 0-250  mA drr	mA dm <sup>-2</sup> ; Ni 1 <sup>-2</sup> ; Ni cathode	. cathode; Ni sacrif 3; Ni sacrificial ano	icial anode; stirrin de; stirring. React	g. Reactions ions made in

<sup>c</sup>Cetyltrimethylammonium bromide

<sup>d</sup>Fractal nickel pressed powder electrodes

°The products were: dihydrocarvone, dihydrocarveol, carvacrol and carvomenthone

<sup>f</sup>The products were: dihydrocarvone, carvotanacetone, carvomenthone, neocarvomenthol, carvomenthol, isocarvomenthol, neoisocarvomenthol

entry 4). The presence of cucurbit[5]uril leads to an enhance of 9% in hydrogenation yields when compared to the control reaction (Table 4, entry 3). The presence of cucurbit[5]uril in the ECHSA process was more efficient than others well establish ECH methodologies described in the literature [48, 50] (Table 4, entries 5–7). The efficiency of selective (S)-(+)carvone hydrogenation was also evaluated by the relation of (SOL + SONE) and (SOL + UOL), where SOL, SONE and UOL are the hydrogenations yield of the saturated alcohol, saturated ketone and unsaturated alcohol. The (SOL+SONE) represents the selectivity for C=C bond hydrogenation and the (SOL+UOL) means selectivity for C=O bond hydrogenation. From the data shown in Table 4 (entry 4), it is observed that the use of cucurbit[5]uril leads to the selective hydrogenation of the C=C bond. This happens, according to the literature, firstly due to the thermodynamics favors the hydrogenation of the C=C bond over the C=O bond by c.a.  $35 \text{ kJ mol}^{-1}$  [51] and second, the C=C bond shows higher reactivity than the C=O bond [52]. Conversely, in the absence of cucurbit[5]uril, the selectivity for C=O hydrogenations increases being this fact related to the extent of the reaction time and/or the catalyst type employed in the experiments.

1-Acetyl-1-cyclohexene, which contains an exocyclic carbonyl was also hydrogenated in presence of cucurbit[5]uril producing 1-acetylcyclohexane (SONE), as the major product and, 1-cyclohexenyl-ethanol (UOL) and 1-cyclohexylethanol (SOL) as minor products (Table 4, entry 9). The presence of cucurbit[5]uril increased by 12% the hydrogenations yields when compared to the control reaction (Table 4, entry 8). The efficiency of selective C=C bond hydrogenation was also evaluated by the ratio of (SOL+SONE)/ (SOL+UOL). The lower the value of the ratio, the higher selective for C=O bon hydrogenation. In this sense, the ratio in the hydrogenation using cucurbit[5]uril (Table 4, entry 9, 4.53 of ratio) was lower than those obtained using fractal nickel pressed powder electrode (Table 4, entry 10, 46.0 of ratio) [53] and Ni electrode in water:methanol system (Table 4, entry 11, 31.3 of ratio) [54] showing the increase of selective C=O bond hydrogenation. This achievement is an important milestone once, as previously cited, the C=C bond react slighter than the C=O bond. Thus, the presence of the cucurbit[5]uril in ECHSA of 1-acetyl-1-cyclohexene, in some manner, seems to favor the hydrogenation of the C=O bond, proving the efficiency, effectiveness and the potential of the use of cucurbit[5]uril as IPTC in ECHSA process.

# Conclusions

Although both cucurbit[*n*]urils and cyclodextrins were known for more than a century, their use as IPTC in electrochemical processes is recent. Hence, the cucurbit[*n*]urils chemistry and its applications have barely been exploited. In this work the interaction behavior of isophorone with cucurbit[n]urils was studied by both cyclic voltammetry and UV/vis spectroscopy. Significant enhancement in both the absorbance peaks and the cathodic current peak of isophorone was attributed to the host-guest complexation with cucurbit[n]urils. In the ECHSA methodology, the use of cucurbit[n]urils as IPTC increase of the solubility of  $\alpha,\beta$ -unsaturated ketones favoring the probability of reaction among the adsorbed substrate in the cathode matrix and the chemisorbed hydrogen leading to an increase of the hydrogenation yield.  $\alpha$ -cyclodextrin and  $\beta$ -cyclodextrin showed better results than those obtained with cucurbit[n]urils being this behavior related with the size of the cavity portal of the cavitands. However, the presence of cucurbit[n]urils in the ECHSA process showed more efficient and selective than others well-establish ECH methodologies described in the literature. In this sense, cucurbit[*n*]urils are primed to play an active role in the development of new IPTC on the electrocatalytic hydrogenation field.

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#### **Compliance with ethical standards**

Conflict of interest The authors declare no conflict of interest.

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