



## Electrochemical studies of irreversibly adsorbed ethyl pyruvate on Pt{*h k l*} and epitaxial Pd/Pt{*h k l*} adlayers

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### ABSTRACT

Cyclic voltammetry (CV) has been used to investigate the irreversible adsorption of ethyl 2-oxopropanoate (ethyl pyruvate (EtPy)) on well-defined Pt and Pd electrodes. Following dosing of EtPy at open circuit on Pt and Pd surfaces, adsorption was found to be structure sensitive with extensive chemisorption being exhibited at {1 1 0} and {1 0 0} terraces together with {1 1 1} × {1 0 0} and {1 1 1} × {1 1 1} steps. However, only very limited adsorption of EtPy was observed at {1 1 1} terraces under identical dosing conditions. In particular, Pt{1 0 0} terraces were found to give rise to significant decarbonylation of molecularly adsorbed EtPy in the hydrogen underpotential deposition (H upd) potential region to generate chemisorbed CO. This finding concerning EtPy adsorption and decomposition agrees with previous investigations on polycrystalline Pt. In contrast, no electrochemical evidence for EtPy decomposition to form adsorbed CO on Pd was ever detected, irrespective of the surface crystallography of the electrode. EtPy decarbonylation was found to be suppressed on Pt{1 0 0} by pre-modification with (R)-[(4S, 5R, 7S)-5-ethenyl-1-azabicyclo[2.2.2]octan-7-yl]-quinolin-4-yl methanol (cinchonidine (CD)), often applied as a chiral modifier in the Pt-catalysed enantioselective hydrogenation of  $\alpha$ -ketoesters. The degree of inhibition was found to be proportional to the amount of CD adsorbed. This surface sensitivity suggested that EtPy requires a very specific adsorption geometry or number of free Pt sites to undergo decarbonylation. For all surfaces studied, EtPy adsorption products could readily be removed either by electrochemical hydrogenation (leaving behind a clean metal surface) or, in the case of adsorbed CO, by performing potential excursions to 0.85 V (Pd/H) to facilitate electrooxidation of CO to CO<sub>2</sub>. The results highlight the relative importance of 'active' {1 1 0} and {1 0 0} defect sites (relative to {1 1 1} terraces) for the chemisorption of EtPy on polycrystalline Pt catalysts used in the enantioselective hydrogenation of  $\alpha$ -ketoesters and this finding may have wider implications for catalyst design methodologies.

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### 1. Introduction

There is increasing interest in the efficient manufacture of fine chemicals whilst limiting environmental impact and cost [1–3]. Of the utmost importance to the pharmaceutical [4–6], agrochemical [7] and fragrance industries [8] is the production of optically active compounds in high enantiopurity, thus making the manufacture of such compounds of huge economic importance. Of the several procedures [9] currently available for manufacturing chirally pure chemicals, chiral catalysts provide perhaps the best means of producing enantiomerically pure compounds [10,11] since only small amounts of the chiral catalyst are required to produce large amounts of the high value chiral compounds, making them both cost effective and environmentally friendly [9,10,12].

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Significant progress has already been made in the area of enantioselective homogenous catalysis [13], which was reflected in 2001 when Sharpless [14], Knowles [15] and Noyori [16] were awarded the Nobel Prize for chemistry for their work on chiral catalysed oxidation and hydrogenation reactions. Numerous transition metal complexes containing chiral ligands have been developed and are widely used in industry for the production of optically pure compounds [9,17].

Although great understanding has been attained already concerning the mechanism of such chemical transformations using homogeneous catalysis, such insights remain a challenge to workers studying reactivity at solid surfaces. Enantioselective heterogeneous catalysis has lagged behind, in spite of the many potential advantages it could yield. These advantages centre on the ease of separation, reuse and the stability of the catalyst, making them ideally suited for large scale industrial processes [18]. One of the greatest challenges therefore is to control the enantioselectivity of a chemical reaction occurring at a solid surface [19].

In this category of surface reaction, the elucidation of the mechanism of the enantioselective hydrogenation of activated  $\alpha$ -keto-esters using cinchona-modified Pt catalysts [20,21] remains a benchmark by which our understanding of chiral heterogeneous catalysis in general may be measured [22–26].

Although several models have been proposed to explain the mechanism of enantioselection under reaction conditions [9,22,27–31] no one theory appears to account satisfactorily for all of the unusual experimental features of this complex surface reaction, for example; the rate acceleration associated with the modified hydrogenation reaction [32–39], its solvent dependency [40–44], the effect of modifier [31,41,45–64] and substrate [52, 64–66] structure and concentration [37,39] together with catalyst preparation [67–72].

In the present study, we focus on the structure sensitivity of the adsorption of the substrate ethyl pyruvate (EtPy) onto well-defined Pt and Pd surfaces since the surface morphology of the Pt catalyst is one feature of this enantioselective heterogeneous reaction that has received only limited attention in comparison [24,26,28,73–77]. With respect to catalyst morphology, early work demonstrated an inverse correlation between enantiomeric excess and Pt dispersion [73], and some investigators proposed a key role for corner atom sites in achieving enantioselectivity [28]. High ee values (ca. 97%) were reported for 1.4-nm colloidal Pt particles [74] again suggesting that suitable edge sites might be of importance, but 0.7-nm silica-supported Pt clusters were inactive [75] probably because of the difficulty of co-adsorbing both modifier and reactant on such finite size restricted surfaces. Thus, the potential of morphology to influence chiral outcome has been recognised.

Cyclic voltammetry is uniquely suited to addressing questions of surface morphology and preferential site adsorption since the various hydrogen underpotential deposition (H upd) voltammetric peaks observed using Pt electrodes in aqueous acidic media may be ascribed unambiguously to adsorption of solution species at particular terrace and step sites [24,26,76–80]. Absence of these singular peaks from a CV following the adsorption of an organic molecule (or a metal/non-metal) is indicative of preferential chemisorption of the molecule at a particular site [78–81].

Previous studies of pyruvate behaviour on Pt have shown that both chemisorbed EtPy and MePy are unstable and undergo various reactions on the Pt surface. Bonello et al. have reported STM, NEXAFS and XPS [82–84] results in UHV which showed that MePy polymerises on Pt{1 1 1} in the absence of co-adsorbed hydrogen. The mechanism for polymerisation was thought to involve deprotonation of the MePy monomer followed by aldol condensation, with the irreversible loss of methanol. The polymerisation reaction was found to be completely suppressed by co-adsorbed hydrogen. It was proposed that catalyst deactivation during start up of enantioselective hydrogenation of alkyl pyruvates may be caused by hydrogen starvation which results in the polymerisation of the substrate.

UHV studies by McBreen et al. using RAIRS, STM and TPD also observed side reactions between adsorbed MePy substrate molecules on Pt{1 1 1} [85]. However, in contrast to Bonello et al. [82–84] they suggested that MePy undergoes a keto-enol driven self-assembly in the absence of sufficient hydrogen coverage leading to reversible H-bonded superstructures on the Pt{1 1 1} surface. It should be noted that NEXAFS did not detect alkene bonds in the polymer [83] as would be expected in such a hydrogen bonded network.

An ATR-IR study by Ferri et al. [86] reported on the fate of EtPy adsorbed on alumina-supported Pt films and on a commercial 5 wt.% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in the presence and absence of co-adsorbed cinchonidine. The study revealed that in the absence of cinchonidine and in the presence of a hydrogen saturated solvent (CH<sub>2</sub>Cl<sub>2</sub>), EtPy readily decomposed producing strongly adsorbed

CO and other fragmentation products on the surface. This agreed with a RAIRS study by Castonguay et al. [87] who also observed MePy decarbonylation on Ni{1 1 1} in UHV. The CO was thought to be adsorbed preferentially on energetically favoured edge and corner sites. When cinchonidine was added, CO was rapidly displaced from the surface. It was also found that EtPy decomposition was suppressed by pre-adsorbed cinchonidine, whereas CO from solution could still be adsorbed. This indicated that EtPy required an ensemble of Pt surface atoms to undergo decomposition, which could not easily be attained when cinchonidine was present on the surface.

The adsorption geometry of molecularly adsorbed EtPy on Pt has also been investigated. Burgi et al. [88] investigated EtPy adsorption on Pt{1 1 1} in UHV using XP and UP spectroscopy, in which it was found that EtPy chemisorption was dominated by a lone-pair orbital interaction between the EtPy carbonyls and the Pt surface. This bonding mechanism indicated that EtPy adopts a perpendicular or tilted (as opposed to parallel) orientation with respect to the surface plane. Furthermore the study also demonstrated that the ketone carbonyl was more strongly involved in the chemisorption than the ester carbonyl. A subsequent *in situ* XANES (UHV) study by Burgi et al. [89] has also been utilised to investigate the adsorption of EtPy in the presence and absence of hydrogen. In the absence of hydrogen it was found that EtPy was preferentially orientated perpendicular to the surface, indicating the predominance of a lone-pair bonding interaction. In the presence of hydrogen the orientation is tilted more towards the surface, in which condition it is thought that EtPy also interacts with Pt via its  $\pi$  system.

In the present study, evidence is presented which demonstrates the surface structure sensitive nature of EtPy adsorption on Pt and epitaxial Pd monolayers on Pt, and in agreement with previous studies, that EtPy undergoes decarbonylation on Pt surfaces.

## 2. Experimental

Pt single crystals were oriented, cut and polished from small single crystal beads (2.5 mm diameter) as described previously [24]. Pt metals used to manufacture the single crystal electrodes were supplied by Goodfellow Metals Ltd. (>99.999% purity). These electrodes were flame-annealed and then cooled in a H<sub>2</sub> atmosphere followed by immersion into ultra-pure water and transfer to the electrochemical cell to form a meniscus contact with the electrolyte [25]. It has been shown that this treatment leads to the production of clean, well-ordered Pt surfaces [26]. The following stepped and kinked Pt single crystal surfaces have been investigated in addition to the basal planes:

$$\begin{aligned}\{11, 1, 1\} &= 6\{100\} \times \{111\} \\ \{533\} &= 4\{111\} \times \{100\} \\ \{755\} &= 6\{111\} \times \{100\} \\ \{976\}^R &= 6\{111\} \times 3\{100\} \times \{110\}\end{aligned}$$

Electrochemical experiments were carried out in a conventional three-electrode cell described previously [90] and all potentials are quoted versus a Pd/H reference electrode in contact with the electrolyte solution. Oxygen was eliminated from the cell by bubbling N<sub>2</sub> into the electrolyte for 20 min. All electrolytes were prepared using 18.2 M $\Omega$  cm Milli-Q water and Aristar grade H<sub>2</sub>SO<sub>4</sub>.

Pd single crystal films were prepared as follows. After verifying the surface order and electrolyte cleanliness by CV, the Pt electrode was rinsed with ultra-pure water and placed briefly in a small beaker containing an approximately 10<sup>-4</sup> M Pd(NO<sub>3</sub>)<sub>2</sub> aqueous solution. The electrode, covered with a small droplet of solution, was then transferred to a bubbler where hydrogen (BOC Gases

99.995%) was continuously bubbled for about 5 s to deposit Pd onto the surface. This deposition procedure was repeated until a film of sufficient thickness was obtained (typically 10–15 dips equated to approximately 15 monolayers of Pd). The electrode was then returned to the electrochemical cell for further experimentation. After measurements were completed, flame annealing the Pd modified electrode for a minute and cooling in hydrogen resulted in the voltammetric characteristics of the platinum single crystal surface being completely restored. A 5% Pt/graphite heterogeneous catalyst (low surface area graphite, with a Pt surface area of  $2.1 \text{ m}^2 \text{ g}^{-1}$  and a mean Pt particle size of 14 nm; supplied by Johnson Matthey) was also used in these studies in order to make comparison with single crystal measurements. This catalyst was sintered for 4 h at 700 K under an atmosphere of 5%  $\text{H}_2$  in Ar prior to electrochemical investigation, in order to generate highly faceted, well-defined platinum nanoparticles and to clean the surface. This results in a reduction in available Pt surface area by a factor of 1.5. The supported platinum catalyst has been described and characterised previously and is known to give rise to sharp, intense voltammetric peaks in the H upd potential region [78]. The working electrode was formed by placing a sample of the sintered catalyst onto a flame-annealed Pt mesh electrode attached to a Pt contact wire.

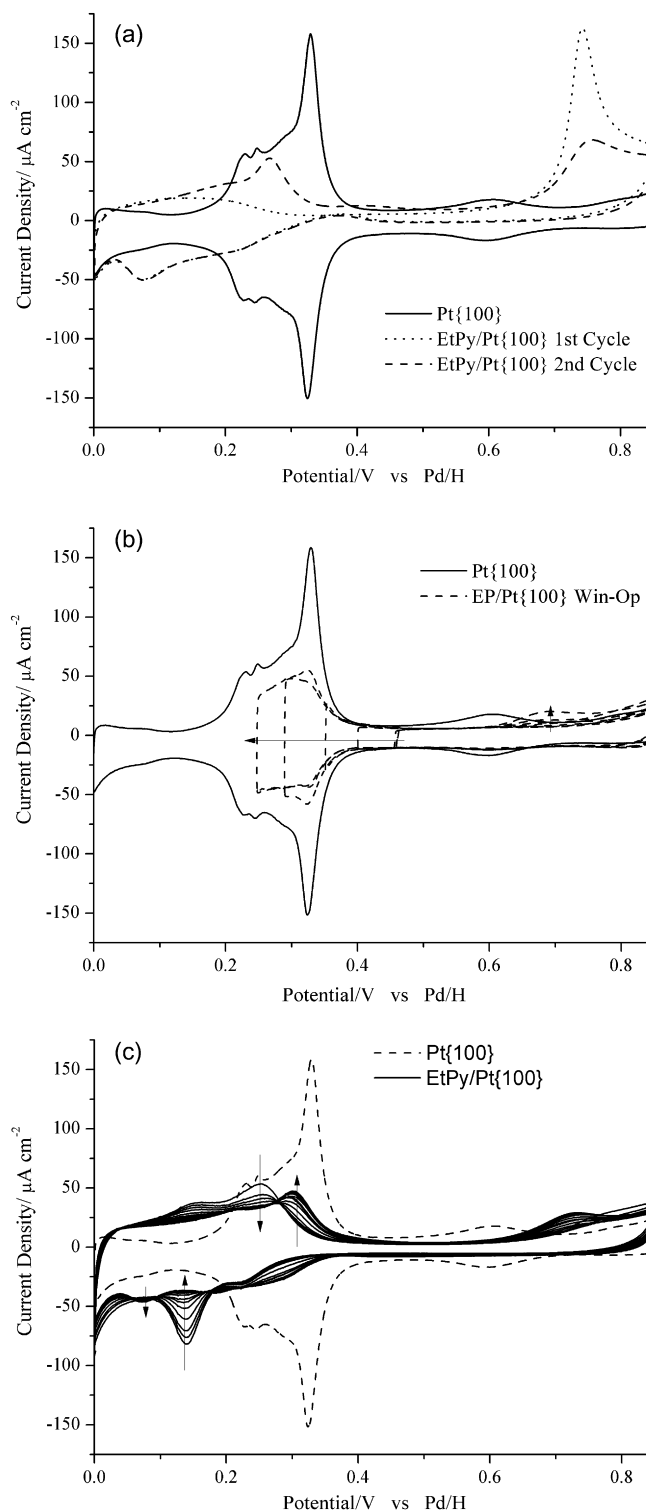
Adsorption of EtPy (Fluka >97% puriss.) was achieved by immersing the working electrode into a neat sample of distilled EtPy for a specified time period to vary coverage. It was then rinsed with ultra-pure water to remove excess EtPy and placed in meniscus contact with the electrolyte. Occasionally, the electrode was transferred (without washing) directly to the electrochemical cell in order to obtain higher coverages of EtPy.

Hydrogen-induced desorption of EtPy could be carried out simply by holding the electrode potential at  $-0.1 \text{ V}$  (Pd/H) to evolve hydrogen gas. Previous electrochemical studies by Vago et al. [91] have demonstrated that hydrogen evolution at palladium electrodes causes EtPy to be converted to ethyl lactate (as measured by HPLC). Modification of Pt with cinchonidine was achieved in an electrochemical cell via irreversible adsorption from a  $5 \mu\text{M}$  solution of cinchonidine (Fluka >98%) in  $0.1 \text{ M H}_2\text{SO}_4$ . Potential cycling in the H upd region was used to monitor the uptake of cinchonidine.

### 3. Results and discussion

#### 3.1. Adsorption of ethyl pyruvate on platinum

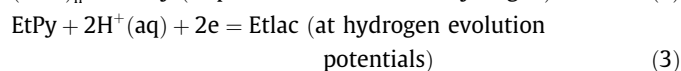
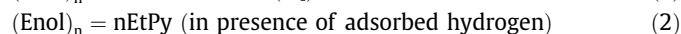
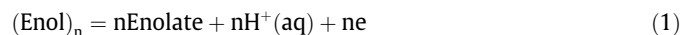
Fig. 1a shows CVs of Pt{1 0 0} before and after dosing with EtPy. The clean surface CV is typical of Pt{1 0 0} electrodes exhibiting good  $(1 \times 1)$  long range order (intense reversible peaks at  $0.33 \text{ V}$  (Pd/H)) and minor contributions from steps (peaks at  $0.23 \text{ V}$  (Pd/H) [78, 92–94]. Several new electroadsorption features were observed after dosing with EtPy. The first sweep (started at  $0.05 \text{ V}$ ) indicated a large reduction in the current associated with the H upd region (potential range from  $0.0 \text{ V}$  to  $0.35 \text{ V}$ ) [79] as vacant surface sites became blocked after exposure to EtPy. This sweep also revealed a large peak at  $0.74 \text{ V}$  which could be ascribed to the electrooxidation of CO, a known decomposition product of EtPy on Pt [86]. These same authors found that CO preferentially bound to energetically favoured step and corner sites on the Pt/ $\text{Al}_2\text{O}_3$  catalyst tested. Other authors have reported similar observations of EtPy decomposition on both Pt [37, 95–97] and Ni [87,98]. In order to establish the potential range in which adsorbed CO was forming, a series of potential window opening experiments were performed (displayed in Fig. 1b). After EtPy adsorption, a potential sweep from  $0 \text{ V}$  to  $0.85 \text{ V}$  was performed to reproduce the CO electrooxidation peak. The potential was then swept towards more negative poten-



**Fig. 1.** (a) Cyclic voltammograms of Pt{1 0 0} together with the first two cycles recorded following the adsorption of ethyl pyruvate at open circuit potential. The electrode was washed prior to transfer to the electrochemical cell. Meniscus contact was then established at  $0.05 \text{ V}$ , (b) a potential window opening study. (c) stripping of ethyl pyruvate by potential cycling (unwashed sample). Electrolyte =  $0.1 \text{ M H}_2\text{SO}_4$ , sweep rate =  $50 \text{ mV s}^{-1}$ .

tials followed by sweeping positive again to observe whether or not adsorbed CO had formed. It was found that so long as the negative-going potential sweep did not reach into the H upd region, no CO electrooxidation would be observed on the subsequent positive sweep. However, when the potential was swept into the H upd

region and subsequently swept towards positive potentials, a CO electrooxidation peak would be observed. This indicates that decarbonylation requires either the adsorption of upd hydrogen or the desorption of anions (which also takes place in this potential range) [99] thus freeing up Pt sites for EtPy decomposition. It may also be that the negative potential itself facilitates decarbonylation. Fig. 1c shows the CV of EtPy obtained without rinsing off excess EtPy with water. The first positive going sweep from 0 V gives rise in this instance to a large voltammetric peak at 0.25 V which we ascribe to a redox process involving the enol – EtPy ((Enol)<sub>n</sub>) self-assembly structures [82–85] formed at room temperature in the absence of adsorbed hydrogen:



After repetitive potential cycles, both this peak and its' related peaks at 0.14 V and 0.07 V (ascribable to the reverse process of Eq. (1)) are seen to decrease in magnitude. The peak at most negative potentials on the negative-going sweep (0.07 V) only emerges after all of the 0.14 V and 0.25 V peak intensities have been dissipated (presumably due to diffusion of excess EtPy away from the stationary electrode surface into the electrolyte). We therefore tentatively suggest that the peaks at 0.07 V, 0.14 V and 0.25 V correspond to adsorption/desorption of self-assembled keto-enol EtPy structures in addition to the EtPy chemisorption layer described in Fig. 1a. The adsorption peak at 0.07 V would then correspond to a very low amount of adsorbed molecular EtPy, perhaps contained in the first layer of EtPy attached to the chemisorbed EtPy layer. Proof of this interpretation awaits further spectroscopic investigation. However, both Lavoie et al. [85] and Bonello et al. [82] observe that adsorbed molecular pyruvate at room temperature following gas-phase dosing of EtPy on Pt forms such a 'polymeric structure'. In the absence of excess EtPy, it is emphasised that all peaks ascribable to self-assembly vanish from the CV and only site blocking by chemisorbed EtPy fragments is observed (Fig. 1a).

Evidently, the decomposition reaction of EtPy on Pt to give CO (seen also in Fig. 1b) must also produce other fragments and intermediates which will be present on the surface and which may contribute to the blocking of H upd features in the CV. It was also apparent that the magnitude of the CO electrooxidation peak was also sensitive to the number of available Pt sites, i.e., the first potential sweep following exposure of the clean Pt electrode always gave rise to the largest CO electrooxidation peak. As Pt sites became more and more occupied by chemisorbed EtPy, it was found that the CO peak would decrease in magnitude. This suggests that the decomposition of EtPy on Pt{1 0 0} to form adsorbed CO requires an ensemble of Pt sites sufficiently large to allow formation of the necessary transition state facilitating decomposition. We shall see later that by blocking Pt sites with adsorbed cinchona alkaloid, a similar deduction may be made.

Fig. 2 shows a CV of Pt{1 1 0} before and after EtPy was irreversibly adsorbed (and excess material rinsed off using water). The intense peak observed in the clean CV at 0.086 V resulting from H upd on Pt{1 1 0} terraces was attenuated markedly after the surface became blocked by EtPy. Only a very weak, broad signal arising from the electrooxidation of CO could be observed in the EtPy/Pt{1 1 0} CV. Hence, in contrast to data shown in Fig. 1, Pt{1 1 0} appears to exhibit a much lower propensity towards decarbonylation of adsorbed EtPy in comparison with Pt{1 0 0}. However, similarly to what was found for Pt{1 0 0}, incomplete blocking of all H upd sites by EtPy was observed with approximately 60–70% of these sites being occupied by adsorbed EtPy according to measure-

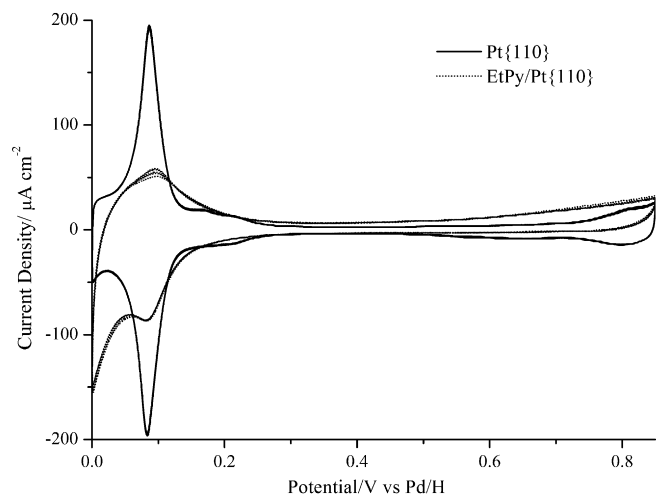


Fig. 2. Cyclic voltammogram of Pt{1 1 0} electrode and the CV recorded following the adsorption of ethyl pyruvate at open circuit potential. The electrode was washed prior to transfer to the electrochemical cell. Meniscus contact was then established at 0.05 V. Electrolyte = 0.1 M H<sub>2</sub>SO<sub>4</sub>, sweep rate = 50 mV s<sup>-1</sup>.

ments of H upd charge before and after adsorption. The onset of a significant reduction current at potentials more negative than 0.05 V when EtPy is adsorbed we ascribe to hydrogenation of adsorbed EtPy.

Fig. 3 shows CVs of EtPy adsorbed on a Pt{1 1 1} single crystal before and after the surface was exposed to a neat solution of EtPy for 5 s and 60 s. The CV taken after EtPy exposure for 5 s shows a small reduction in the H upd current with a further similar decrease after 60 s. The sharp spike characteristic of well-ordered Pt{1 1 1} electrodes in sulphuric acid at 0.44 V is heavily attenuated in both of the EtPy dosed CVs. In contrast to Fig. 1 however, CV indicated that even after 60 s exposure to EtPy, only a small proportion of the Pt{1 1 1} surface became blocked by EtPy. It is evident that the majority of the {1 1 1} surface remained free of adsorbed EtPy. Furthermore, no oxidation or reduction peaks corresponding to EtPy decomposition products were observed. From Figs. 1–3, it may be concluded that EtPy preferentially adsorbs on Pt{1 0 0} and Pt{1 1 0} sites and that decomposition of EtPy to CO occurs mainly on Pt{1 0 0}.

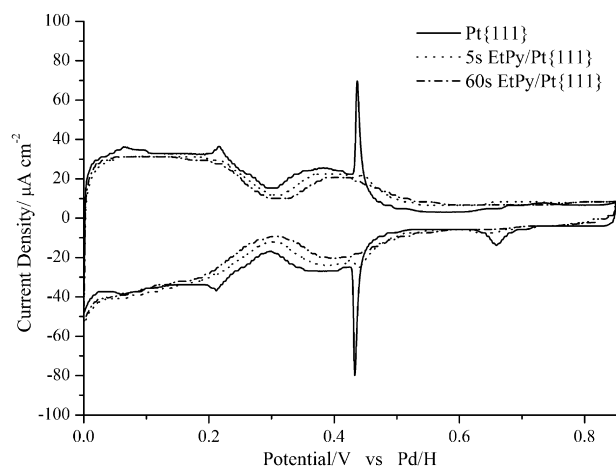


Fig. 3. Cyclic voltammogram of Pt{1 1 1} and the CV recorded following the adsorption of ethyl pyruvate. The electrode was washed prior to transfer to the electrochemical cell. Meniscus contact was then established at 0.05 V. Dosing was carried out for different lengths of time as indicated in the legend. Electrolyte = 0.1 M H<sub>2</sub>SO<sub>4</sub>, sweep rate = 50 mV s<sup>-1</sup>.

The possibility of site selective adsorption by EtPy was explored further using stepped platinum electrodes as shown in Fig. 4. Fig. 4a shows CVs of EtPy irreversibly adsorbed on Pt{11, 1, 1}, after dipping the single crystal into neat EtPy for 5 s and 10 s. The Pt{11, 1, 1} surface consists of six atom wide {1 0 0} terraces (indicated by the current peak at 0.33 V) separated by {1 0 0} × {1 1 1} steps (indicated by the sharp peak at 0.22 V) [24,26,76–78]. The sweep after 5 s of EtPy exposure revealed a significant attenuation in both the 0.33 V and 0.22 V peaks. After 10 s exposure, there is a further decrease in the current signals at 0.33 V and 0.22 V. At this stage the {1 0 0} terraces appear to be almost completely blocked with EtPy whereas some of the {1 0 0} × {1 1 1} step sites remain vacant. As the {1 0 0} terraces on the Pt{11, 1, 1} surface become increasingly filled with EtPy from 5 to 10 s there is a corresponding increase in the magnitude of the signal between 0.60 V and 0.75 V caused by the electrooxidation of decarbonylation products formed at the Pt{1 0 0} terrace sites (see Fig. 1). The size of the CO electrooxidation peak is significantly decreased in relation to that observed in Fig. 1 and we suggest that this is because the surface density of Pt{1 0 0} terrace sites is reduced compared to Pt{1 0 0}.

Fig. 4b shows the CV of EtPy adsorbed on Pt{5 3 3}, a surface which contains four atom wide {1 1 1} terraces separated by {1 1 1} × {1 0 0} step sites [78]. After 5 s exposure to EtPy, the signal at 0.22 V (associated with the {1 1 1} × {1 0 0} step sites) was heavily attenuated whereas the weak signal between 0.45 V and 0.55 V (associated with the {1 1 1} terraces) remained unchanged. The attenuation of the signal at 0.22 V was caused by selective blocking of step sites by EtPy and the absence of a change in the signal between 0.45 V and 0.55 V suggested that the {1 1 1} terraces remained largely unoccupied in the presence of EtPy. This CV further demonstrates the surface sensitive nature of EtPy adsorption, with adsorption occurring preferentially on ‘{1 0 0} type step’ sites over {1 1 1} terrace sites. In addition, the absence of Pt{1 0 0} terraces appears to afford negligible adsorbed CO as signified by the presence of only a weak, broad electrooxidation feature at 0.7 V.

Fig. 4c shows a CV of a Pt{9 7 6}<sup>R</sup> single crystal before and after EtPy adsorption. The Pt{9 7 6}<sup>R</sup> is a chiral surface consisting of {1 1 1} terraces and kinks composed of {1 1 0} and {1 0 0} steps. A large decrease in the current signal at 0.06 V and 0.20 V was observed after initial EtPy exposure as the kink and step sites became heavily blocked with EtPy. Only a slight decrease in the signal between 0.33 V and 0.55 V was observed as the {1 1 1} terraces were only partially occupied by EtPy. In fact after stripping of the small amount of adsorbed CO formed on the positive going sweep, the reverse sweep indicated an increase in charge in the Pt{1 1 1} terrace anion peak. Hence the small amount of blocking observed initially for {1 1 1} terrace sites may be ascribed almost entirely to adsorbed CO, not EtPy. The significant attenuation in the current signals associated with {1 1 0} and {1 0 0} step sites coupled with the absence of an attenuation in the {1 1 1} terrace signal provided further evidence for the surface sensitive nature of EtPy adsorption proposed.

### 3.2. Adsorption of ethyl pyruvate onto epitaxial adlayers of palladium

Fig. 5a shows a CV of EtPy adsorbed on an epitaxial Pd/Pt{1 0 0} adlayer overlaid on the CV of the corresponding clean Pt{1 0 0} single crystal. The Pd/Pt{1 0 0} CV indicates that the single crystal surface contains both first and second layer Pd regions as signified by intense H upd signals at 0.12 V [100,101] and 0.23 V [102,103] respectively. The CV after the 1st EtPy exposure resulted in a significant reduction in the H upd current as the Pd{1 0 0} surface became blocked with EtPy. In particular, the second layer Pd sites were seen to be occupied prior to those corresponding to Pd in the first adlayer immediately adjacent to Pt{1 0 0}. There was a fur-

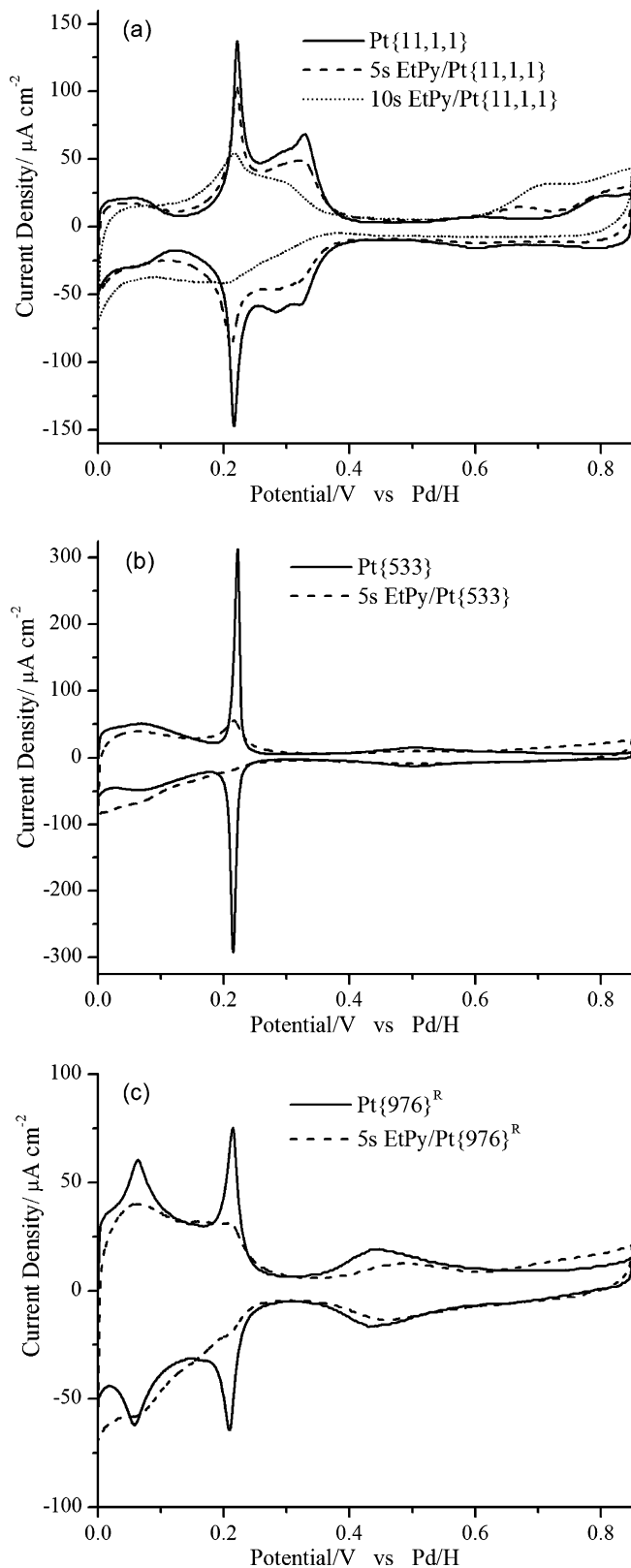
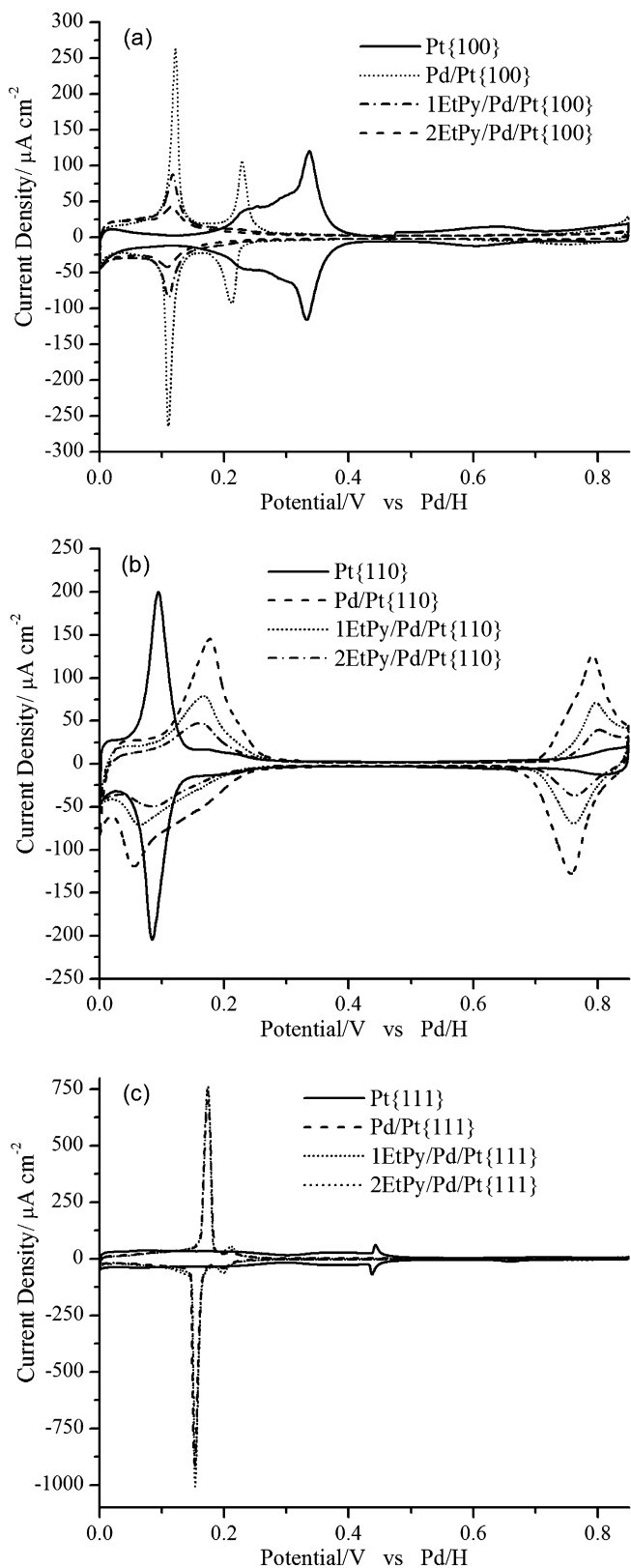


Fig. 4. CVs of (a) Pt{11, 1, 1}, (b) Pt{5 3 3} and (c) Pt{9 7 6}<sup>R</sup> before and after the adsorption of ethyl pyruvate. The electrodes were washed prior to transfer to the electrochemical cell. Meniscus contact was then established at 0.05 V. Dosing times are provided in the legend. Electrolyte = 0.1 M H<sub>2</sub>SO<sub>4</sub>, sweep rate = 50 mV s<sup>-1</sup>.

ther reduction in the charge in the H upd region after the 2nd exposure of EtPy as more vacant sites in the first Pd monolayer became occupied, leading to over 70% of H upd sites becoming



**Fig. 5.** Voltammetric profiles for epitaxial palladium adlayers supported on (a) Pt{1 0 0}, (b) Pt{1 1 0} and (c) Pt{1 1 1}, together with the profiles recorded following the adsorption of ethyl pyruvate. The electrode was washed prior to transfer to the electrochemical cell. Meniscus contact was then established at 0.05 V. The integers displayed in the legend indicate the number of times ethyl pyruvate was dosed onto the surface. Electrolyte = 0.1 M H<sub>2</sub>SO<sub>4</sub>, sweep rate = 50 mV s<sup>-1</sup>.

blocked with EtPy after this exposure. In contrast to Fig. 1, signals resulting from the oxidation of CO and/or other EtPy decomposi-

tion products were not observed in the Pd/Pt{1 0 0} CV though EtPy was clearly present on the surface. The absence of this signal suggests that EtPy does not undergo decarbonylation on Pd{1 0 0} (as it does on Pt{1 0 0}). This indicates that the decarbonylation reaction of EtPy is both structure sensitive and metal sensitive.

Fig. 5b is a CV of EtPy adsorbed on an epitaxial Pd/Pt{1 1 0} adlayer overlaid on the CV of the clean Pt{1 1 0} single crystal. The signal at 0.18 V corresponding to H up on the 1st layer Pd/Pt{1 1 0} [101] decreased progressively after the 1st and 2nd EtPy exposures, as the surface became increasingly blocked by EtPy. The signal at 0.79 V attributed to Pd-oxide formation at high potentials [101] also decreased after the 1st and 2nd EtPy exposures as the amount of free surface Pd capable of forming the oxide layer decreased. The CV after the 2nd dip indicated there was a near-complete monolayer coverage of EtPy with only 15–20% of H up sites free. Again, as for Pt{h k l}, complete blocking of all H up sites could not be realised even after extensive EtPy exposure. In addition, no evidence of EtPy decomposition to adsorbed CO on Pd could be observed using CV.

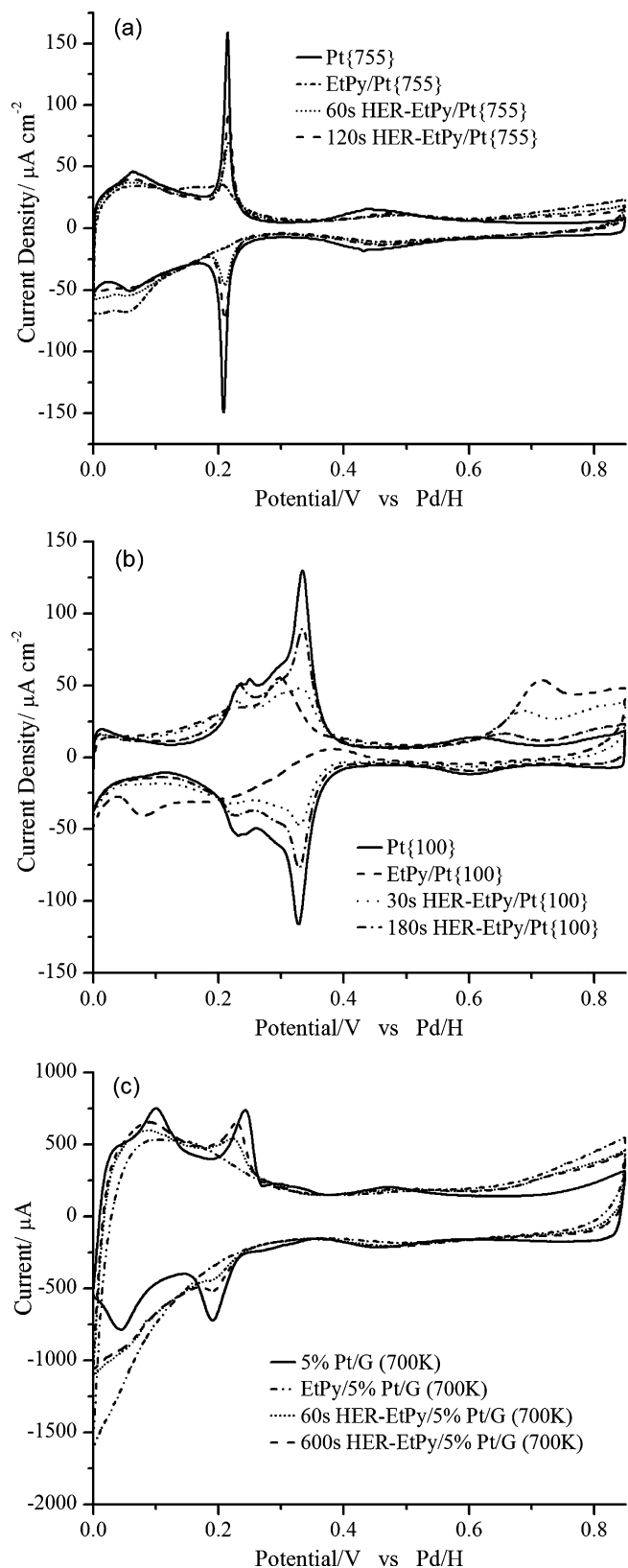
Fig. 5c is a CV of EtPy adsorbed on an epitaxial Pd/Pt{1 1 1} adlayer overlaid on the CV of the clean Pt{1 1 1} single crystal. The current signal at 0.17 V is associated with hydrogen adsorption on 1st layer Pd{1 1 1} [104–106]. Regions of second layer palladium are also visible at 0.23 V. There was no change in the signal at 0.17 V after two exposures to EtPy, indicating that the number of vacant surface sites remained virtually unchanged.

These data indicate that EtPy adsorption on Pd/Pt{h k l} show the same dependency on surface morphology as adsorption on Pt{h k l}. EtPy adsorbs readily on the Pd{1 0 0} and {1 1 0} surfaces, whereas no adsorption was observed on the epitaxial Pd{1 1 1} surface. Fig. 5 also demonstrated the relative stability of molecular EtPy on Pd in contrast to Pt, whereby EtPy readily decomposed to produce adsorbed CO and other fragments on the surface which were observed electrochemically at potentials greater than 0.6 V.

### 3.3. Hydrogen-induced desorption of ethyl pyruvate

Fig. 6a shows the effect of holding the working electrode at hydrogen evolution potentials (HEP) after dosing EtPy on a Pt{7 5 5} single crystal. The Pt{7 5 5} surface consists of six atom wide {1 1 1} terraces (signified by the broad signal between 0.35 V and 0.55 V) separated by {1 0 0} × {1 1 1} steps (signified by the sharp spike at 0.22 V) [78]. The signal at 0.22 V was heavily attenuated in the EtPy/Pt{7 5 5} CV as {1 0 0} × {1 1 1} step sites became blocked with EtPy. However, there was only a small decrease in the signal between 0.35 V and 0.55 V suggesting that the terraces remained largely vacant under the same exposure conditions. Once again EtPy exhibited a strong adsorption affinity for the {1 0 0} × {1 1 1} step sites. After the electrode was held at HEP for 60 s an increase in the current at 0.22 V was observed as EtPy was removed from the surface and {1 0 0} × {1 1 1} step sites were liberated. A further increase was observed in the current at 0.22 V after 120 s at HEP as more {1 0 0} step sites became vacant. There was a negligible dependence of the current between 0.35 V and 0.55 V with respect to the length of exposure to HEP, since the {1 1 1} terraces remained largely vacant throughout the entirety of the experiment.

Fig. 6b shows the effect of holding the working electrode at HEP for different time periods of EtPy dosing on a Pt{1 0 0} single crystal. After exposure to HEP for 30 s, {1 0 0} surface sites became liberated as indicated by the increasing current signal at 0.33 V. A further increase in the current is observed after 180 s at HEP as the majority of the {1 0 0} sites became vacant and a relatively clean surface was obtained. Corresponding to these changes in EtPy coverage on the surface there was a decrease in the current



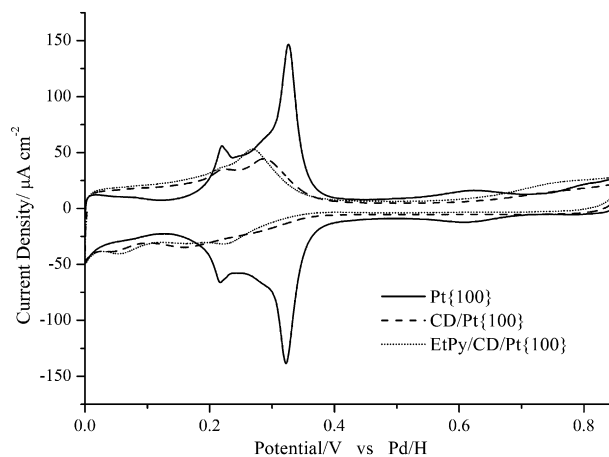
**Fig. 6.** Cyclic voltammograms showing the change in coverage of ethyl pyruvate on (a) Pt{755}, (b) Pt{100}, and (c) 5% Pt supported on graphite, after holding the potential at  $-0.1$  V (Pd/H) for different lengths of time. No transfers or washing of the electrodes were involved. Electrolyte =  $0.1$  M  $\text{H}_2\text{SO}_4$ , sweep rate =  $50$   $\text{mV s}^{-1}$ .

at  $0.75$  V and  $0.08$  V as decarbonylation and residual EtPy fragments were removed from the surface.

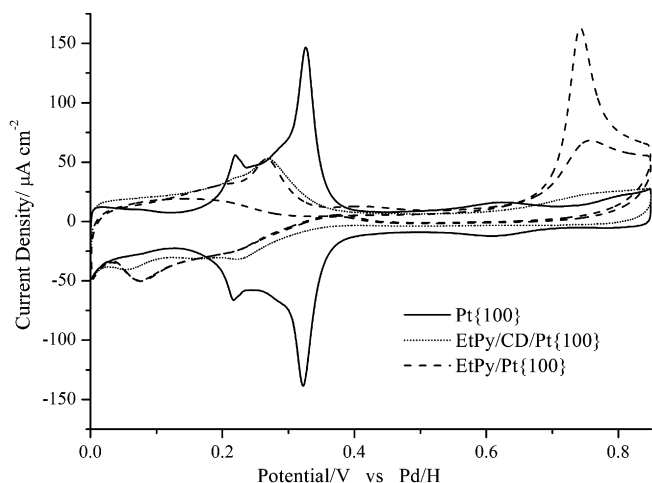
Fig. 6c is a CV of EtPy adsorbed on 5% Pt supported on graphite showing the effect of exposure of the electrode to HEP for different time intervals. After exposure to EtPy, the 5% Pt/G CV revealed a reduction in the current at  $0.10$  V (corresponding to  $\{110\}$  sites) and likewise at  $0.24$  V (corresponding to  $\{100\}$  step sites), whereas there was little change in the current between  $0.40$  V and  $0.50$  V (corresponding to  $\{111\}$  terrace sites). In accordance with previous figures this was attributed to the selective blocking of  $\{110\}$  and  $\{100\}$  surface sites whilst  $\{111\}$  sites remained largely unoccupied. The result obtained in this ‘real’ catalyst reinforces previous results obtained from single crystals which strongly indicate the surface sensitive nature of EtPy adsorption on Pt and Pd and the fact that chemisorbed EtPy may be removed from the surface (presumably as ethyl lactate) under hydrogen evolution conditions. Further inspection of Fig. 6c in particular also indicates that, of the sites previously occupied by EtPy, there appears to be no preferential desorption of hydrogenated product at hydrogen evolution potentials, i.e. both  $\{100\}$  terrace sites and  $\{110\}/\{100\}$  step sites appear to lose EtPy at equal rates.

#### 3.4. The effect of pre-modifying Pt{100} with cinchonidine on EtPy decomposition

To investigate the effect that cinchonidine (CD) would have on both the adsorption and decomposition of EtPy, EtPy was adsorbed on a Pt{100} surface pre-modified with CD. Fig. 7 shows a CV of CD on Pt{100} (after CD had been adsorbed onto the surface according to the experimental procedure outlined in Section 2.) upon which a CV of EtPy on CD/Pt{100} is overlaid. In contrast to EtPy adsorption on non-modified Pt{100} (as shown in Fig. 1), CD appeared to significantly suppress EtPy decomposition to adsorbed CO. Evidence that EtPy was present on the CD pre-modified surface may be gleaned both from the presence of the very small CO peak at  $0.74$  V when EtPy is co-adsorbed with CD and from inspection of the electroadsorption peaks at  $0.27$  V (positive sweep) and  $0.22$  V (reverse sweep) which are identical in potential to the analogous peaks observed in the absence of CD (see Fig. 8). These peaks were never observed with singly adsorbed CD on Pt{100}. Fig. 8 is an overlay of the CVs of EtPy on modified and non-modified Pt{100} emphasising the coincidence in potential of EtPy induced electroadsorption peaks when singly adsorbed and co-adsorbed with CD. The slight shift towards negative potentials of the  $0.07$  EtPy peak in the presence of CD (Fig. 8) is also apparent. Again, this peak is more intense than the one at similar potential observed with just



**Fig. 7.** Cyclic voltammograms of cinchonidine on Pt{100} and ethyl pyruvate on cinchonidine modified Pt{100} after ethyl pyruvate adsorption at open circuit. The electrode was washed prior to transfer to the electrochemical cell. Meniscus contact was then established at  $0.05$  V. Electrolyte =  $0.1$  M  $\text{H}_2\text{SO}_4$ , sweep rate =  $50$   $\text{mV s}^{-1}$ .



**Fig. 8.** Cyclic voltammograms comparing ethyl pyruvate adsorption on non-modified and cinchonidine modified Pt{100}. Electrolyte = 0.1 M H<sub>2</sub>SO<sub>4</sub>, sweep rate = 50 mV s<sup>-1</sup>.

singly adsorbed CD. It was found that the amount of CO formed by EtPy was a function of CD coverage in that as CD coverage was increased, the magnitude of the CO decomposition peak also decreased. Since neither CD nor EtPy can block all Pt sites [78] no complete adsorbed monolayer was formed by CD. An electrochemical study of CD adsorption on polycrystalline Pt by Bakos et al. [107] found the maximum CD coverage to be 50% and indeed from Figs. 7 and 8, free platinum sites are still available after dosing. This suggests that the present results may be interpreted within a geometric model whereby EtPy decomposition to adsorbed CO requires a certain ensemble size of surface sites. If this were not the case then EtPy should decompose to give CO on these 'free' Pt sites to give a CO peak at least as intense as that shown in Fig. 1a (second cycle) since the number of 'free' H up sites is approximately the same. This conclusion is supported by an FTIR spectroscopy study by Liu et al. [96] which found that both gas-phase H<sub>2</sub> and co-adsorbed CD could significantly suppress the decomposition of EtPy on Pt/γ-Al<sub>2</sub>O<sub>3</sub>. Furthermore, an ATR-IR study of EtPy adsorption on Pt/Al<sub>2</sub>O<sub>3</sub> films and commercial powder Pt/Al<sub>2</sub>O<sub>3</sub> catalysts by Baiker and co-workers [86] found that CD rapidly displaced CO from the surface when CD was added after EtPy decomposition had taken place. Furthermore, on modified Pt, CD was found to effectively suppress EtPy decomposition. The authors proposed that the decomposition of EtPy requires a considerable ensemble of free Pt surface sites, which could not be achieved in the presence of CD. The observations were used to explain the dependency of the cinchona-modified Pt catalytic system on the sequence of admission of reactant and modifier to the reaction system [108]. It was predicted that the CO poisoning resulting from EtPy decomposition would affect the catalytic behaviour and contribute to the initial transient period [23,95] observed with these hydrogenation reactions. The present study concurs with these findings.

#### 4. Conclusions

EtPy adsorption on Pt{*hkl*} and epitaxial Pd/Pt{*hkl*} adlayers monitored by CV has been reported. EtPy adsorption was found to be highly dependant on surface morphology. The present voltammetric studies found that EtPy adsorbed preferentially on {100} and {110} sites on both Pt and Pd often leading to high coverages of surface intermediates. Adsorption of EtPy was disfavoured on {111} terraces of both Pt and Pd.

CV studies also found that EtPy readily decomposed on Pt{100} producing adsorbed CO and other (unknown) fragments on the

surface, which are oxidised at more positive potentials. Interestingly, no decarbonylation could be observed using Pd surfaces. Hence, decarbonylation was also found to be highly surface sensitive. The reaction was mainly observed on Pt{100} terraces. EtPy decarbonylation is suppressed on Pt{100} surfaces pre-modified with cinchonidine. As reported previously by Ferri et al. [86], we find that decarbonylation requires a certain Pt atom ensemble size in order to occur and the action of CD appears to be to decrease the Pt ensemble size available for EtPy adsorption.

The present study clearly demonstrates the dependency of EtPy adsorption and its stability on surface morphology. It is therefore imperative that catalyst morphology is considered as an important parameter in discussions concerning the rate enhancement and enantioselectivity (and other empirical features) of the 'Orito reaction'. The result also has implications concerning catalyst design methodologies. It can be postulated that increasing the number of active {100} and {110} sites on the catalyst surface would increase the amount of EtPy adsorbed. However, it may be that increasing the number of {100} terraces on the catalyst would also facilitate more EtPy decomposition towards adsorbed CO.

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