

Displacement of Ethene and Cyclohexene from Polycrystalline Pt and Pt(110) Electrodes

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The adsorbate formed after adsorption of cyclohexene on Pt(110) and polycrystalline Pt electrodes is displaced by competitive adsorption of UPD copper. Since it desorbs as benzene, cyclohexene is dehydrogenated during adsorption. After adsorption of ethene on polycrystalline Pt, only 10% of the adsorbate are displaced by Cu, leaving the surface as ethene. This corresponds to weakly adsorbed species, probably π -bound ethene.

Introduction

It is one of the challenges of modern electrochemical surface science to clarify to what extent the adsorption at the metal–electrolyte interface resembles that at metal surfaces in a vacuum. The adsorption of ethene at metal surfaces is one of the most frequently studied systems in heterogeneous catalysis. Therefore, it is of interest to study its adsorption also at the metal–electrolyte interface. A comparison should give information about the influence of the electrolyte on the adsorption reaction. Besides, in electrochemistry a better understanding of the adsorption behavior of small organic molecules should help in optimizing electrocatalysts for various purposes, such as fuel cells, sensors, and electrosynthesis.

Various species have been identified on Pt surfaces after ethene adsorption from the gas phase:^{1–4} at low temperatures a di- σ -bound species is formed, which transforms to ethylidene at room temperature. Recently, also a π -bound ethene has been found, which is the intermediate during gas phase hydrogenation.⁵ The adsorption of cyclohexene from the gas phase has been studied due to its potential relevance as intermediate during hydrogenation of benzene. A comparison with the adsorption of ethene is also interesting because of the steric hindrance. Cyclohexene has been found to decompose above 200 °C to benzene on Pt(111) and Pd(111).^{6–9}

An early comparison between these two interfaces (metal/gas and metal/electrolyte) dealing with the adsorption and the hydrogenation behavior of ethene appeared in 1985.¹⁰ Using a special transfer system between the electrochemical environment and UHV, the adsorption of various other unsaturated organic compounds on a Pt(111) electrode was studied by Auger electron spectroscopy and electron energy loss spectroscopy.^{11–13}

The electrochemistry of ethene at porous, polycrystalline Pt was one of the first systems studied by differential electrochemical mass spectrometry (DEMS).¹⁴ We have recently reported on measurements with DEMS using single-crystal electrodes,^{15–17} which show that ethene forms various adsorbate states also at the metal electrolyte interface: A C₂ species (probably associatively adsorbed ethene), which predominates at Pt(110) and at low adsorption potentials, can be cathodically desorbed as ethane and butane. A second adsorbate state (possibly ethylidene) predominating at the Pt(111) face can only be desorbed oxidatively as CO₂. A third species, predominately formed at fairly positive potentials, decomposes at low potentials to methane and adsorbed CO and is presumably a (C–C–O) entity.

In the case of adsorbed cyclohexene on a Pt(111)-electrode surface, electrochemical and mass spectrometric results indicate that an oxygenated species similar to the case of adsorbed ethene is also formed. On Pt(110) and a polycrystalline electrode, however, adsorbed cyclohexene behaves very similarly to adsorbed benzene. During a potential sweep into the hydrogen region, it is desorbed largely as cyclohexane and, to a minor degree, as benzene.^{17,18}

Due to the hydrogenation reaction occurring at low potentials, some information about the adsorbate itself is lost. We therefore tried to achieve a less drastic desorption of the adsorbate species by displacing them by other strongly adsorbing species in the double layer region. This procedure was first tested with adsorbed benzene.¹⁹ These experiments showed that benzene can be displaced largely by adsorbing Cu²⁺ as underpotential deposited (UPD) Cu from a Pt(110) and a polycrystalline Pt electrode.

Using C₆D₆ as adsorbent on polycrystalline Pt, it was shown that no H/D exchange occurs during adsorption: during displacement by UPD Cu, C₆D₆ was the only desorbing species observed. This proves that the H/D exchange observed during desorption of benzene in the hydrogen region (leading primarily to the hydrogenated product cyclohexane) occurs during desorption.

In a previous paper,²⁰ we have already reported that ethene adsorbed on polycrystalline Pt can only be partially displaced: Cu, I[–], and CO were used as displacing agents and all of them led to the desorption of only approximately 10% of the adsorbate. A similar result was obtained when displacing ethene from a porous, polycrystalline Pd electrode by iodine, whereas the use of CO or Cu led to coadsorption.

Here, we extend this study to the displacement of cyclohexene on a polycrystalline Pt and a Pt(110)-electrode and present further results on the displacement of ethene.

Experimental Section

The differentially pumped mass spectrometer system has been described in previous papers.²¹ The quadrupole mass spectrometer was a Balzers QMG 511.

Two different electrochemical cells were used. For most experiments with polycrystalline electrodes, a conventional DEMS cell was used, where the working electrode consists of a porous Teflon membrane, onto which the electrocatalyst is sputtered. This membrane separates the electrolyte and the vacuum of the mass spectrometer. The geometric surface area

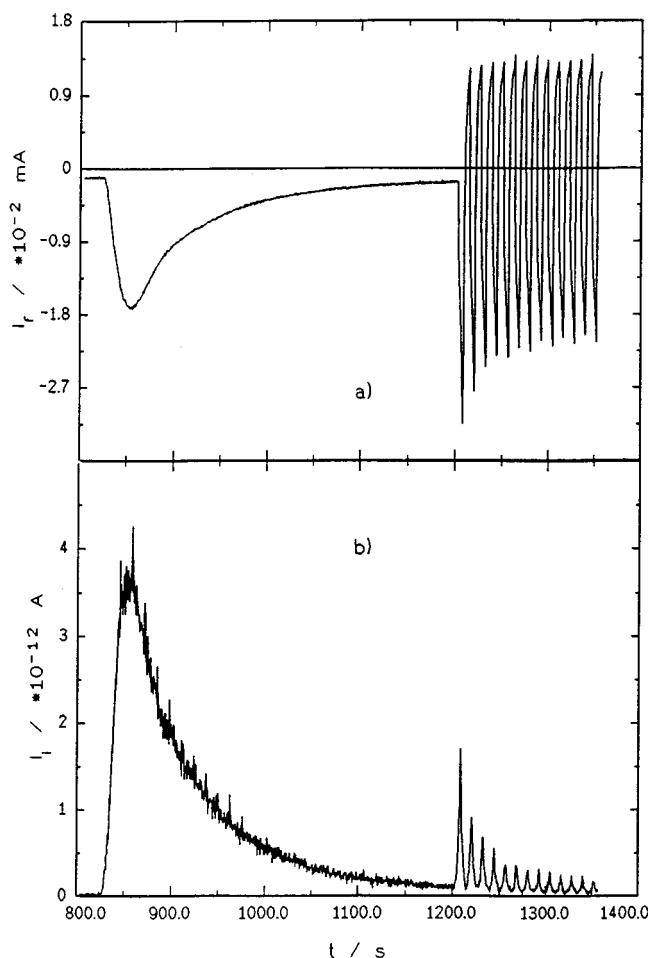


Figure 1. Displacement of adsorbed cyclohexene from porous polycrystalline Pt at 0.4 V by UPD Cu in 10^{-4} M Cu^{2+} solution: (a) current transient; (b) ion current for $m/z = 78$. At $t = 1200$ s, potential sweeps between 0.25 and 0.5 V were applied ($\nu = 12.5$ mV/s).

is 0.5 cm^2 and the roughness factor around 15. Volatile species formed at the electrocatalyst diffuse through the pores to the vacuum side of the membrane. For measurements with smooth electrodes and single crystals, a thin layer cell was used.^{16,22} Here, the electrodesorption products diffuse through the thin layer of electrolyte between the electrode and an uncovered Teflon membrane, which again separates the electrolyte from the vacuum. The geometric surface area of the electrode is 0.28 cm^2 . Two counter electrodes were used, positioned at the electrolyte inlet and the outlet. The reference electrode was a normal hydrogen electrode.

Single-crystal electrodes were prepared by annealing in a hydrogen flame, cooling in a pure Ar stream, and immersing in the supporting electrolyte ($0.5 \text{ M H}_2\text{SO}_4$). During the transfer into the thin layer cell they were protected by a droplet of electrolyte. Cleanliness was checked by cyclic voltammetry in the thin layer cell prior to the experiment.

Ethene and cyclohexene were adsorbed as follows: Cyclohexene was adsorbed at the smooth electrodes by flushing $0.5\text{--}1 \text{ mL}$ of a $4 \times 10^{-4} \text{ M}$ cyclohexene solution in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte through the thin layer cell at 0.4 V for 2 min. After an adsorption time of 4 min altogether, the electrolyte was exchanged by the supporting electrolyte. At the porous electrode, adsorption was performed by introducing H_2SO_4 saturated with cyclohexene into the cell so that the total concentration rendered $4 \times 10^{-4} \text{ M}$. Ethene ($5.5 \times 10^{-3} \text{ M}$ in $0.5 \text{ M H}_2\text{SO}_4$) was adsorbed at 0.4 V at Pd and at 0.3 V at Pt by flushing the electrolyte with ethene for 4 min. After adsorption, a complete

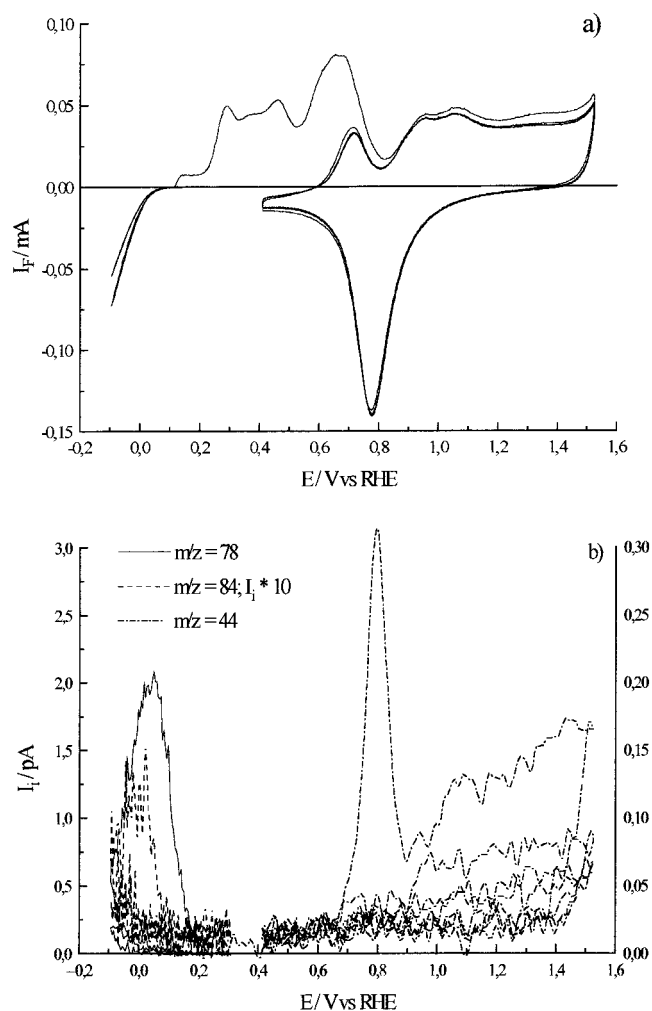


Figure 2. CV (a) and MSCV (b) after displacement of adsorbed cyclohexene on porous polycrystalline Pt by Cu^{2+} in the supporting electrolyte ($\nu = 12.5$ mV/s; $0.5 \text{ M H}_2\text{SO}_4 + 10^{-4} \text{ M CuSO}_4$).

electrolyte exchange was performed in both cell types. The mass spectrometer was calibrated for all species via a leak valve.^{23,24} In addition, before each experiment it was calibrated for CO_2 by oxidation of CO adsorbed at a polycrystalline electrode. Taking into account pseudocapacitive effects which amount to 20% of the oxidation charge.²⁵ These values were used to adjust the calibration constants obtained with the calibration leak. The determined coverages were reproducible to within $\pm 15\%$.

Results

Cyclohexene. Cyclohexene adsorbed at the porous Pt electrode was displaced by introducing a Cu^{2+} solution into the cell at 0.4 V so that the resulting concentration was 0.1 mM . Cu^{2+} adsorption lead to the current transient shown in Figure 1a. After 10 min, additional potential sweeps were performed between 0.4 and 0.25 V to achieve a more complete desorption. Simultaneously, mass spectrometric ion currents were recorded for $m/z = 80, 82, 84$, and 78. An increase was only observed for $m/z = 78$ (Figure 1b); therefore, only benzene was desorbed during Cu adsorption; no cyclohexene, cyclohexadiene, or cyclohexane was detected during Cu adsorption. Integration of the ion current transient yielded a charge corresponding to a change of coverage $\Delta\Gamma = 0.1 \text{ nmol/cm}^2$. During the additional potential sweep another 0.01 nmol/cm^2 were desorbed. (The spikes at $t > 1200$ s in the current and in the ion current transient are due to these sweeps.) An even more complete desorption was achieved when after the displacement the electrolyte was

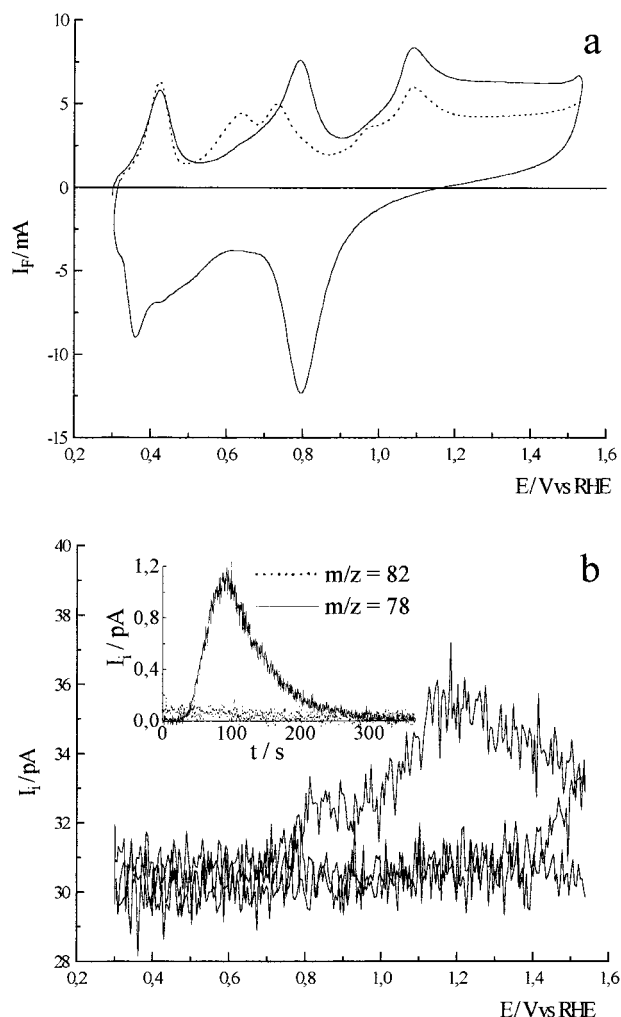


Figure 3. CV (a) and MSCV (b) for CO_2 ($m/z = 44$) during the potential sweeps in positive direction after displacement of adsorbed cyclohexene from Pt(110) ($v = 12.5$ mV/s; 0.5 M $\text{H}_2\text{SO}_4 + 10^{-4}$ M CuSO_4). Inset: ion current transients for benzene and cyclohexene during displacement.

again exchanged for the supporting electrolyte and potential sweeps between -0.1 and 0.3 V were applied (Figure 2). 0.036 nmol benzene was thus detected and also traces of cyclohexane (0.004 nmol/ cm^2) similar to the case of the adsorption of benzene.¹⁹ The peaks in the subsequent cyclic voltammogram are mainly due to the dissolution of Cu. The peak in the MSCV for $m/z = 44$ at 0.8 V might indicate a minor decomposition of the adsorbate to a CO-like species.

A qualitatively identical result was obtained when the adsorbate formed from cyclohexene at the Pt(110) electrode was displaced by injecting 0.1 mM Cu^{2+} electrolyte into the thin layer cell at a flow rate of 0.05 $\mu\text{L/s}$ (cf. Figure 3, inset). By sweeping the potential in a positive direction after this displacement the residual organic adsorbate is oxidized to CO_2 . Therefore, the ion intensity for $m/z = 44$ is a measure for the completeness of the displacement. Figure 3 gives an example and also shows that the UPD Cu peaks typical for Pt(110) at 0.4 and 0.75 V are only slightly disturbed. The results are summarized in Figure 4.

Ethene. Similar experiments were performed with ethene preadsorbed at a porous polycrystalline electrode at 0.3 V. The current transient during copper deposition and the simultaneously detected ion current for $m/z = 26$ are shown in Figure 5. No ion current was observed for $m/z = 30$ and therefore ethene is the only desorption product. Integration of the ion

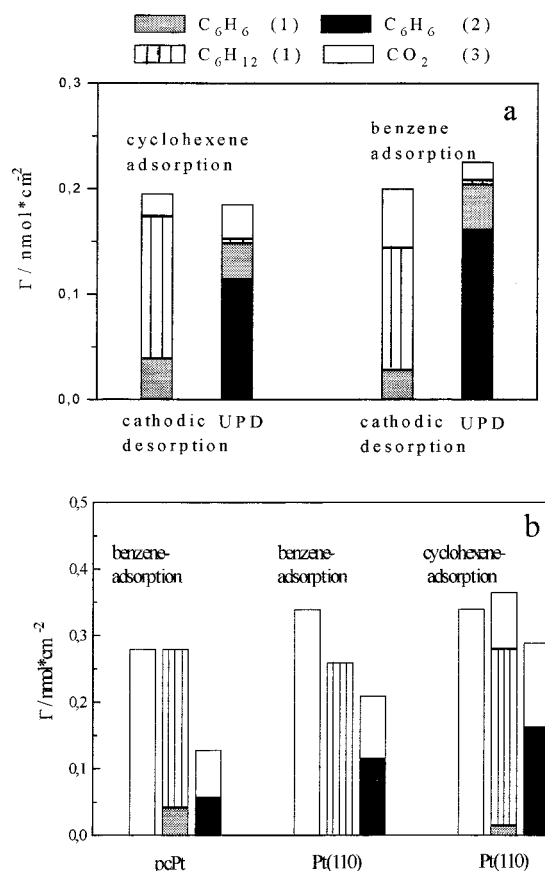


Figure 4. Comparison of the amounts of products observed during displacement with those observed during cathodic desorption after adsorption of benzene and cyclohexene (1 = evolved during cathodic potential sweeps, 2 = displaced by UPD Cu, 3 = found during anodic potential sweep). (a) Porous polycrystalline electrode; (b) smooth Pt electrodes. (left bar) CO_2 evolved during direct oxidation of the adsorbate. (middle bar) Benzene and cyclohexane formed during cathodic potentialsweeps. (right bar) Benzene formed during displacement and CO_2 formed during oxidation of the residual adsorbate.

current transient gives a value of 0.1 nmol/ cm^2 ethene. This corresponds to 14% of the total coverage with ethene, which, by oxidation to CO_2 , was evaluated to be 0.72 nmol/ cm^2 ²⁰ (cf. Figure 5). Integration of the faradaic charge gives a value of 270 $\mu\text{C}/\text{cm}^2$ as compared to a value of 350 $\mu\text{C}/\text{cm}^2$ for a monolayer of Cu.²⁶ The amount of deposited copper is therefore less than a monolayer, but, taking into account the small amount of displaced ethene, seems too large. This high coverage with Cu may be due to the fact that the porous Pt electrode is not saturated by adsorbed ethene, because the ethene concentration during adsorption decreases considerably in the pores due to evaporation. (On Pt(110), a maximum ethene coverage of 1.15 nmol/ cm^2 was found.^{16,17})

In the subsequent anodic sweep the copper-desorption peaks overlap with the onset of the oxidation of the residual ethene (Figure 6). Also, without preceding displacement adsorbed ethene is oxidized in two oxidation peaks to CO_2 , as revealed by the MSCV. The first is due to the oxidation of an oxygen-containing adsorbate; the other has been ascribed to the oxidation of associatively bound ethene or ethylidyne.¹⁷ Only the second wave is diminished after Cu adsorption. The total amount of CO_2 corresponds to an amount of 0.65 nmol/ cm^2 ethene, 0.08 nmol/ cm^2 less than without Cu displacement. This value is close to the 0.1 nmol/ cm^2 of ethene observed in the transient.

As in the case of cyclohexene, a more complete desorption can be achieved by sweeping the potential to -0.1 V after an

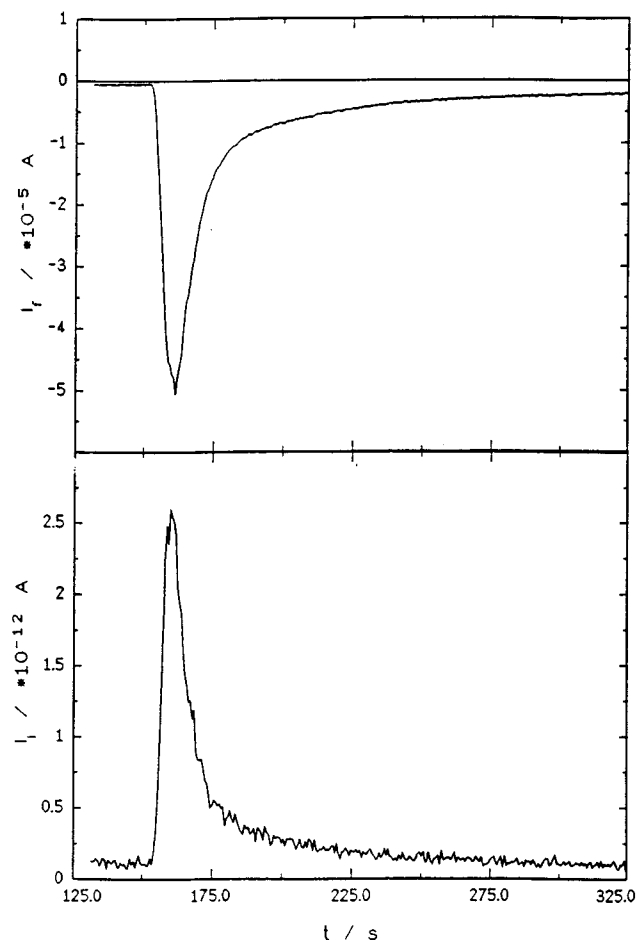


Figure 5. Displacement of preadsorbed ethene from porous polycrystalline Pt at 0.3 V by UPD Cu (10^{-3} M CuSO_4): (a) current transient; (b) ion current transient for $m/z = 26$.

electrolyte exchange to pure sulfuric acid, which is performed to avoid bulk deposition of copper (Figure 7). In this case, also ion currents for $m/z = 15$, 30, and 43 were found in addition to that for $m/z = 26$. Therefore, further displacement of ethene takes place possibly due to further deposition of copper; some copper ions may have survived the electrolyte exchange. In addition, hydrogenation to ethane and dimerization to butane occurs during cathodic potential sweeps with an ethene-covered electrode in pure sulfuric acid, suggesting that the part of the adsorbate, which is not displaced by Cu, retains its chemical identity. (The absence of an ion current for $m/z = 44$ during the cathodic sweeps shows that $m/z = 43$ corresponds to butane and not propane.)

Subsequent oxidation of the residual adsorbate shows that approximately 30% ($0.22 \text{ nmol cm}^{-2}$) of the adsorbate formed originally survive displacement and cathodic desorption. A comparison of Figures 6 and 7 shows that also the additional cathodic desorption takes place at the expense of the second oxidation wave, whereas the amount of CO_2 formed in the first oxidation wave is much less influenced. (Please note that the calibration constant varies from experiment to experiment.) The results are summarized in Figure 8.

Discussion

The adsorbate formed from cyclohexene is largely displaced by Cu and desorbed as benzene. This clearly shows that cyclohexene is dehydrogenated to benzene upon adsorption on a Pt(110) and polycrystalline Pt electrode. The only alternative

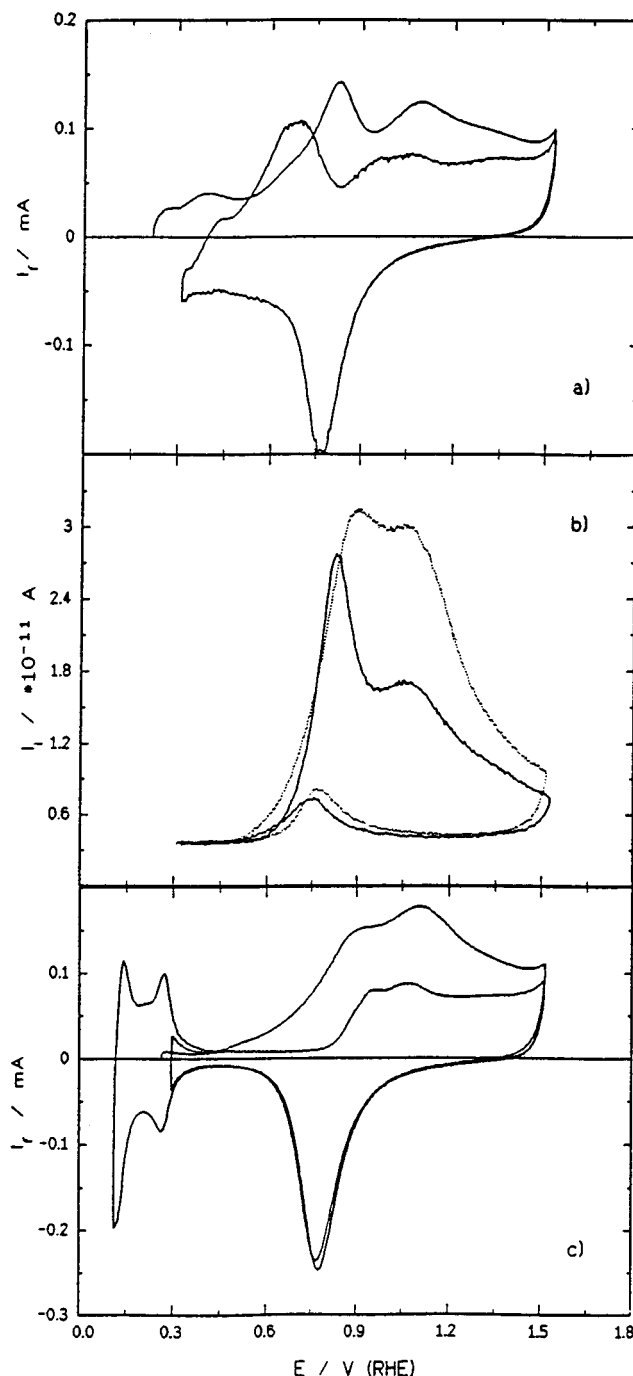


Figure 6. 4.15 CV (a) and MSCV (b) for CO_2 ($m/z = 44$) during the potential sweeps in positive direction after displacement of adsorbed ethene from porous polycrystalline Pt. For comparison, the CV (c) and MSCV (b, dotted line) without previous displacement are also shown.

interpretation, the dehydrogenation during the displacement by Cu, can be ruled out because Cu should rather decrease the catalytic activity of Pt and because some benzene is also formed without Cu deposition during a potential sweep into the hydrogen region.²² However, the behavior on Pt(111) is totally different:¹⁸ there, adsorbed benzene is desorbed as such close to 0.0 V (RHE), whereas the adsorbate formed from cyclohexene is only partially desorbed, yielding benzene, cyclohexene, and cyclohexane, and a species which is probably an oxygenated compound, possibly cyclohexanol.

Similar to both the faradaic hydrogenation of dissolved species and the hydrogenation of adsorbed species during their desorption, the dehydrogenation requires an open surface

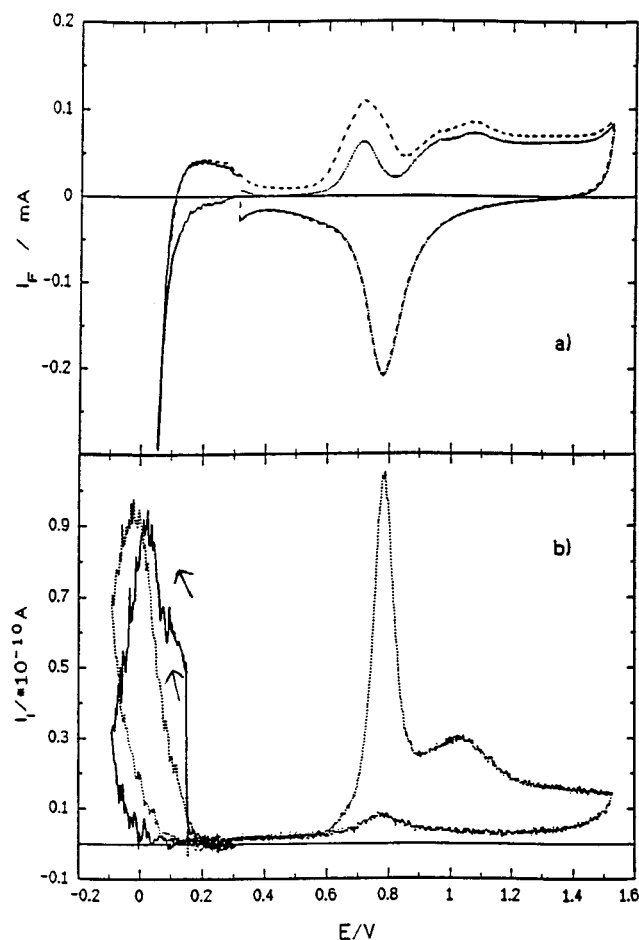


Figure 7. Cathodic desorption of adsorbed species surviving the displacement of ethene by Cu followed by oxidation of the residual adsorption. CV (a) and MSCV (b) for $m/z = 30$ (ethane, straight line), $m/z = 26$ (corrected for the contribution the ethane fragment: ethene, dotted line), and $m/z = 44$ (CO_2).

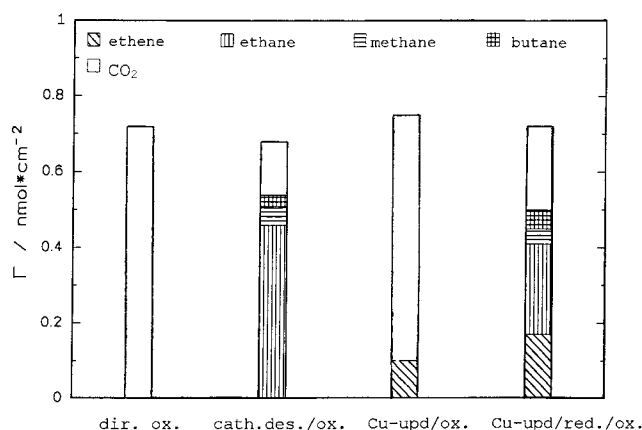


Figure 8. Comparison of the amounts of desorption products of preadsorbed ethene obtained by the various procedures: (a) direct oxidation in an anodic potential sweep; (b) desorption in a cathodic potential sweep to -0.1 V followed by an anodic potential sweep; (c) displacement by UPD Cu followed by an anodic potential sweep; (d) displacement by UPD Cu followed first by a cathodic potential sweep to -0.1 V and then an anodic potential sweep.

structure, stabilizing reaction intermediates in the activated complex. The reaction mechanism can be assumed to be identical to the back reaction of the hydrogenation reaction, the single steps of which have been shown before to be reversible using H/D exchange^{23,24} (except, of course, for the last step involving formation of cyclohexane).

TABLE 1: Comparison of the Transfer Efficiency Values with the Collection Efficiency for CO in the Mass Spectrometric Thin Layer Compartment (See Text for Details)

$u/(\mu\text{L s}^{-1})$	f_{CO}	N_{H_2}	N_{CO_2}	N_{displ}
0.05	≈ 1			0.74
0.08	≈ 1			0.48
0.22	0.8		0.75	0.26
1	0.25	0.95	0.3	
2	0.2	0.75	0.13	

The amounts of desorption products are similar to those obtained after adsorbing benzene. Therefore, as one might expect, the dehydrogenation reaction does not require any extra space. Desorption is almost complete when additional potential sweeps into the hydrogen region are performed. These are necessary because the adsorption of Cu is shifted to lower potentials due to the organic adsorbate. Interestingly, in the anodic sweeps after displacement, a peak for CO_2 formation is visible at 0.8 V in the mass spectrometric cyclic voltammograms, indicating the presence of a CO-like species, which might be formed in a side reaction, possibly catalyzed by Cu. Since the same peak was observed for benzene, it is not related to the probable formation of cyclohexanol on Pt(111).

In the case of the porous polycrystalline electrode, the coverage obtained from the amount of desorption product plus the residual adsorbate as determined from subsequent cathodic or anodic desorption is, within experimental error, identical to that formed by direct oxidation to CO_2 or cathodic desorption. This is different for the smooth electrodes, where the thin layer cell had to be used. Here, the discrepancy between the amounts of displaced products and the coverage determined from the amount of CO_2 during direct oxidation of the adsorbate (or from the cathodic desorption products) shows that some of the displacement products are lost. The reason is obvious: whereas experiments involving potential-induced desorption (anodic and cathodic) are performed under stopped flow and all volatile desorption products reach the Teflon membrane, i.e., the transfer efficiency (ratio of detected product to total product) N is 1, the displacement has to be performed during a constant flow of electrolyte in order to ensure mass transport of the displacing agent (Cu^{2+}) to the surface. Therefore, a part of the desorption product is transported out of the thin layer volume before reaching the Teflon membrane. In Table 1 we compare the transfer efficiencies obtained from the ratio of the detected species to the total amount of displaced species (N_{displ}) to those obtained for hydrogen evolution, CO-oxidation and to the collection efficiency for CO (at open circuit potential). Here, the collection efficiency for CO (f_{CO}) was determined by having the electrolyte (saturated by CO) flow into the thin layer cell; it is calculated from the ratio of the number of moles entering the cell (per unit of time) to that entering the vacuum, as given by I_i/K_0 . The latter value has been shown to be proportional to $u^{1/3}$ as expected for thin layer cells (where u is the flow rate).¹⁷ N_{H_2} is the transfer efficiency for hydrogen during hydrogen evaluation. It is considerably larger than f_{CO} , although smaller values might be expected because H_2 molecules produced close to the outlet of the cell have no chance to reach the Teflon membrane. We assume that a part of the electrolyte passes the thin layer cell at its edges, diminishing the effective flow rate at the center. This leads to lower values of f_{CO} and higher values of N_{H_2} . N_{CO_2} is the ratio of CO_2 molecules entering the vacuum chamber to those produced during continuous faradaic oxidation of CO_2 . This value again is much lower, because the oxidation rate is diffusion-limited and most CO molecules react close to the edge of the thin layer where the flow rate is high and the

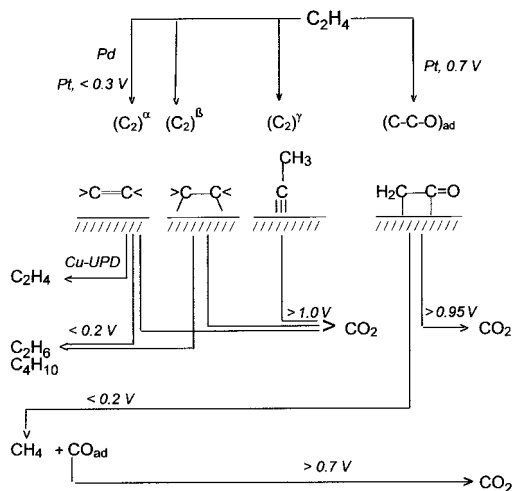


Figure 9. Proposed adsorption and desorption reactions of ethene on Pt and Pd electrodes.

collection efficiency lower than at the center. Much lower than all these values is the ratio of detected benzene to that displaced by Cu (N_{displ}).

A possible reason for this behavior is that the evaporation of benzene is not only diffusion limited, but also kinetically hindered.

Contrary to cyclohexene, only a small part of the adsorbate formed from ethene can be displaced from polycrystalline Pt. The reason for the difference is that, on the one hand, the dehydrogenation of cyclohexene to benzene, which, due to its aromatic stabilization, is associatively adsorbed. On the other hand, ethene is dissociatively adsorbed and leads to a variety of adsorbed states as we have shown before: one state corresponds to that ethene which is cathodically desorbable as ethane and which is predominantly formed at Pt(110) and polycrystalline Pt and Pd, while another state corresponds to that adsorbate which is nondesorbable (possibly ethylidene). A third state is an oxygen-containing species which is formed especially at the higher potential limit of the double layer at Pt (but not at Pd), and which decomposes at low potentials to methane and an adsorbed, CO-like species. The results described above suggest the existence of a further state, which represents the adsorbed ethene which can be displaced not only by Cu, but also by CO and iodine.²⁰ Since this state (now $(C_2)^\alpha$) only amounts to about 10% of the total adsorbate, it is not identical to the state which can be desorbed under hydrogenation to ethane $(C_2)^\beta$. It is rather unlikely that solely due to energetic reasons only 10% can be displaced (unfavorable position of the equilibrium), because all three displacing agents lead to the same result. A comparison of the amounts of species detected by cathodic desorption and by displacement followed by cathodic desorption (Figure 8) suggests that both the $(C_2)^\alpha$ and $(C_2)^\beta$ state can be cathodically desorbed. These reactions are summarized in the reaction sequence shown in Figure 9, which is a modification of that already proposed in ref 17.

Conclusion

Displacing volatile organic adsorbates by other species and their mass spectrometric detection helps in characterizing reactive organic adsorption systems on electrode systems in situ.

Particularly, we could thus demonstrate that cyclohexene is dehydrogenated to benzene upon adsorption on a Pt(110) and polycrystalline electrode and that 10% of the adsorbed ethene on polycrystalline Pt are very weakly bound, possibly via π -bonding.

For quantitative determinations of desorption products from single-crystal electrodes, the cell has to be improved in a way that it can be calibrated independently for the transfer efficiency. We are currently testing the suitability of the cell described in ref 27 for simultaneous DEMS/EQCM measurements.

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