ELECTROCHEMICAL PROCESSES OF ADSORBED CHLOROBENZENE AND FLUOROBENZENE ON A PLATINUM POLYCRYSTALLINE ELECTRODE

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The electrode processes of chlorobenzene (CB) and fluorobenzene (FB) on polycrystalline platinum (Pt-pc) electrode in sulfuric acid were studied by differential electrochemical mass spectrometry (DEMS). Contrary to the oxidation of adsorbed benzene on Pt surface, the oxidation of adsorbed CB and FB in the oxygen adsorption region does not provide solely CO_2 as the final product. At negative polarization potentials CB and FB were desorbed under dehalogenation. While in the case of FB only benzene was detected, CB gave intermediates besides benzene. The final product of stepwise hydrogenation of these species was cyclohexane.
Keywords: Electrochemical degradation; Hydrogenation; Dehalogenation; Fluorobenzene; Chlorobenzene; Differential electrochemical mass spectrometry (DEMS); Cyclic voltammetry (CV).

The reasons for studying the interaction of organic molecules on electrode surfaces, which act as heterogeneous catalysts, are often related to fuel cell research[1]. Electrocatalytic reactions might be of interest in electroorganic synthesis for their detection using electrochemical gas sensors[2,3] and because of their use as corrosion inhibitors or additives in metal plating[4].

Aromatic halogenated hydrocarbons rank among persistent organic pollutants (POPs) due to their toxicity and persistence in the environment. It is very important to study the reactivity and transformation processes of these substances to find a method of their degradation in the environment and conversion to less harmful compounds. Electrochemistry offers possibilities of decomposition of aromatic halogenated hydrocarbons at low temperature in a liquid medium by direct reductive or oxidative processes.

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For example, Farwell and co-workers[5] studied a electrochemical reduction of the C–Cl bond in polychlorinated benzenes in non-aqueous media of dimethyl sulfoxide (DMSO) and showed that gradual electrochemical breaking of the carbon–chlorine bond is the main process.

Electrochemical methods have been rarely used in aqueous solutions because of low solubility of halogenated aromatic compounds. Direct electroreductive breaking of the carbon–halogen bond was often not possible due to very high electron affinities of most halogenated compounds. Therefore, it is necessary to use an indirect electrochemical reduction method.

Connors and Rusling[6] proved that indirect dechlorination occurred at more positive potentials than the direct reduction. Miyoshi and co-workers examined indirect dechlorination of organohalogen compounds by an electrocatalytic cation supply system[7]. Hashimoto and co-workers[8] investigated dechlorination of chlorobenzene in acetonitrile on metal electrodes (Pt, Cd, Sn, In, Pb, Zn, Ag) using naphthalene as a mediator. Meniny and co-workers studied chlorobenzene on Ni/SiO_2 catalyst[9]. The main product of the electrolysis was benzene. Keanea, Murthy and Patterson investigated indirect catalytic hydrodehalogenation (HDH) of fluorobenzene (FB), chlorobenzene (CB), bromobenzene (BB), iodobenzene (IB), 1,3-dichlorobenzene (1,3-DCB), 1,3-dibromobenzene (1,3-DBB) and 1,3-bromochlorobenzene (1,3-BCB) over unsupported and silica-supported Ni at 573 K [10].

We have focused on the process of indirect reductive conversion of aromatic halogenated hydrocarbons based on the replacement of halogen atoms by electrochemically formed hydrogen. Unfortunately, the electrochemical data obtained during cathodic polarisation do not allow direct monitoring of the process due to overlapping of the successive reaction and hydrogen evolution. A very suitable tool for in situ observation of volatile and semivolatile species formed during such transformation processes is DEMS [2,11].

Baltruschat and co-workers intensively studied the oxidative and hydrogenation desorption of benzene and bicyclic aromatic compounds adsorbed on monocrystalline Pt surfaces by DEMS in sulfuric acid[12–14]. They proved that at low and negative potentials, the adsorbed benzene is almost fully hydrogenated on Pt-pc electrode[4].

So far no DEMS studies of electroreduction and electrooxidation of aromatic chloro and fluoro compounds on polycrystalline electrode in acid aqueous solutions have been reported.

EXPERIMENTAL

Chemicals

Suprapure reagents H_2SO_4 (95–97%), C_6H_5F (≥99%) and C_6H_5Cl (≥99%) were purchased from Merck, and benzene of pro analysis quality (p.a.) from Chemapol. Millipore water was prepared by the Milli-Q Plus System (Millipore, USA). All solutions were prepared immediately before the experiment.

Instruments

The experimental set-up showing the electrochemical thin layer cell and its connection to mass spectrometer was described previously[1,15,16]. The mass spectrometer used was a quadrupole Trio 1000 (Finnigan MAT, Fisons Instruments, San Jose, USA) with the mass range m/z 2–1000 and with an electron multiplier as the detector. For all measurements we used the single ion monitoring (SIM) mode, which facilitates more sensitive measurement of 32 selected ions. The CB mass spectrum measured in SIM mode (Fig. 1) corresponds to the spectrum of pure CB from NIST database.

The vacuum connection of the electrochemical thin layer cell with the ion source of the mass spectrometer was provided by a hand-control vacuum valve (Balzers, type EVA 016 HX) and by a sample probe inlet valve, using a home-made stainless construction. A standard electrochemical arrangement of an electrochemical thin layer cell consists of a smooth working Pt-pc electrode, two auxiliary platinum electrodes and a reference reversible hydrogen electrode (RHE) to which all potentials were related. Volatile products from electrochemical reactions diffused within 2–3 s through a thin layer of the electrolyte to the Teflon membrane, where they evaporated. The membrane used was made of PTFE (GoreTex, No. S10570, pore 0.02 µm, thickness 75 µm, porosity 50%). The active area 0.8 cm^2 of the membrane was determined by the area of a supporting porous steel frit SipermR R14, (Tridelta Siperm GmbH, Dortmund, Germany). During the measurements, constant temperature was maintained.

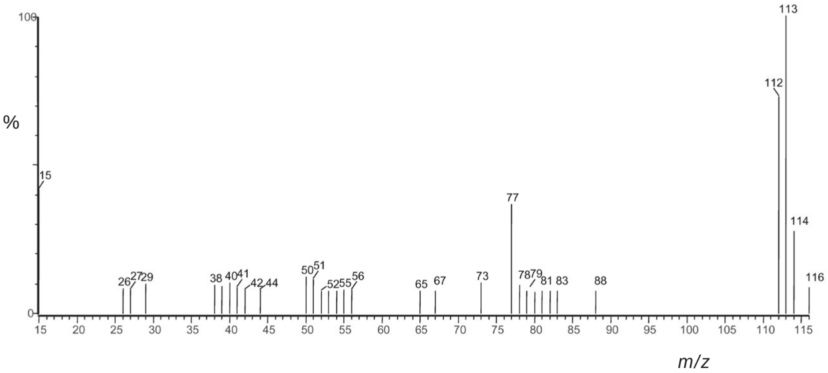


Fig. 1

The mass spectrum (SIM mode) of CB saturated in 0.5 M H_2SO_4 measured at adsorption potential E_{ad} = 0.4 V vs reversible hydrogen electrode (RHE)

Adsorption of Halogenated Benzenes

The adsorption is performed by passing ca. 1 ml of 0.5 M H_2SO_4 saturated with the substance through the thin layer. The saturation concentration was 0.044 M for chlorobenzene and 0.016 M for fluorobenzene. During the whole adsorption time (5 min) the potential was held at adsorption potential E_{ad} = 0.4 V (Fig. 2), which was chosen in the double layer region[11]. After thorough electrolyte exchange with pure supporting electrolyte only the species adsorbed on the electrode remained in the thin layer cell. After adsorption, the potential was swept in the positive direction (oxidation) or negative direction (reduction with cathodic desorption).

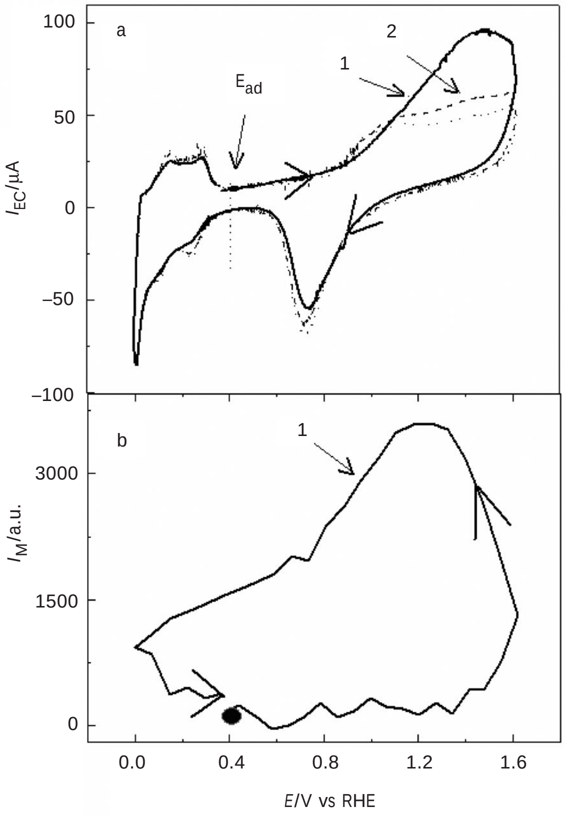


FIG. 2
a Direct oxidation of adsorbed FB in 0.5 M H_2SO_4 on Pt-pc electrode, E_{ad} = 0.4 V vs RHE, scan rate 20 mV s^{-1}, potential step 2 mV, starting potential 0.4 V, cathodic switching potential 0 V, anodic switching potential 1.62 V; the numbers 1, 2 indicate the number of cycles, dotted line represents supporting electrolyte. b Corresponding MSCV curve for *m/z* 44, ● starting potential 0.4 V, arrows indicate the direction of polarization

In a typical DEMS experiment, the ion mass current I_M of specific m/z values corresponding to the given species of interest is recorded in parallel with the faradaic electrode current during the potential sweep, yielding the mass spectrometric cyclic voltammogram (MSCV)[1]. All ion currents shown here are normalized by dividing by the abundance of the fragment[4]. All reference spectra used in this paper have been taken from the NIST Chemistry Web Book 2006 [17]. The transfer charges have been obtained by numerical integration of faradaic current–time data in the potential range 1.00–1.64 V. A correction for the charge of supporting electrolyte in the same potential range has been made.

RESULTS AND DISCUSSION

The objective of our work was to investigate adsorption processes and the reactivity of FB and CB on Pt-pc electrode in order to compare the results with those obtained for benzene, which was hydrogenated in the adsorbed state on Pt-pc electrode[2,12,18–20]. The aim of the work was (a) to investigate whether both FB and CB are dehalogenated during electroreduction and hydrogenated similar to benzene on Pt-pc electrode in acid aqueous solutions and (b) to estimate possible differences between CB and FB processes.

Electrochemical Behavior of Fluorobenzene on Polycrystalline Platinum Electrode

The adsorption potential E_{ad} for FB was 0.4 V (versus reversible hydrogen electrode (RHE)). After the adsorption step (5 min) the potential was swept in positive direction into the oxygen evolution region or in negative direction into the hydrogen evolution region (Figs 2 and 4). The corresponding CV curves and MSCV curves were measured.

Oxidation of Fluorobenzene on Polycrystalline Platinum Electrode

Figure 2 shows the direct oxidation of FB adsorbed on Pt-pc electrode. Comparing the curve of the supporting electrolyte (dotted line), the working scan is characterized: (i) by the broad oxidation peak with the onset at about 0.886 V and with the current maximum I_{max} at 1.47 V, (ii) by a small potential shift of ca 0.01 V of the cathodic peak of Pt oxides reduction which appears at about 0.72 V, (iii) by moderate suppression of both cathodic and anodic currents in the hydrogen adsorption/desorption potential range. The suppression indicates the adsorption of FB on the surface of Pt-pc electrode.

The proof that CO_2 does not leak into the electrochemical cell during the experiment is I–t curve (curve of dependence of ion current on time) for *m/z* 44. Figure 3 shows that certain volume of CO_2 (*m/z* 44) was detected in MS (approx. 300 a.u.) before the start of polarization of the electrode. However, oxidation peak of CO_2 arising during direct oxidation of adsorbed FB in 0.5 M H_2SO_4 was many times higher (approx. 3600 a.u.) and did not originate from CO_2 dissolved in solution.

In comparison with benzene, where the current maximum for oxidation is observed at 1.35 V on Pt-pc electrode[4], the current maximum for FB oxidation is shifted to more positive potentials (1.45 V). The oxidation of FB is complete often three anodic cycles. In these cycles, except for the final product CO_2, also intermediates are formed that are already partially oxidized but remain adsorbed on the electrode. The oxidation thus does not lead solely to CO_2, contrary to the case of adsorbed benzene, which is completely oxidized to CO_2 in the first cycle at potentials where oxygen is adsorbed[14].

Hydrogenation of Fluorobenzene on Polycrystalline Platinum Electrode

Both processes of desorption and hydrogenation of adsorbed FB were studied in the expanding potential range. This means that the starting potential was 0.4 V and switching potentials, consequently, corresponded to 0, –0.1,

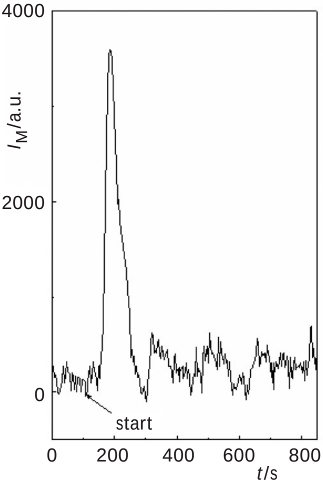


FIG. 3
The dependence of ion current for CO_2 (*m/z* 44) on time. Arrow indicates the start of polarization of Pt-pc electrode in anodic direction. Peak corresponds to CO_2 evolved during direct oxidation of the adsorbed FB in 0.5 M H_2SO_4

–0.17, –0.27 and –0.37 V. The final positive potential remained unchanged and corresponding to 0.7 V.

When the potential is first varied in the negative direction towards the potential 0 V, we indicated potential-dependent I_M for specific *m/z* values (Fig. 4), which are further described below. The MS experiment showed that FB desorbs in the potential region of hydrogen adsorption like benzene (*m/z* 78). At more negative potentials (–0.1 V), where hydrogen evolution occurs, FB was desorbed under full hydrogenation to cyclohexane (*m/z* 84).

DEMS method enables to detect intermediates of electrochemical hydrogenation in both adsorption and flow-through regimes of concentrated so-

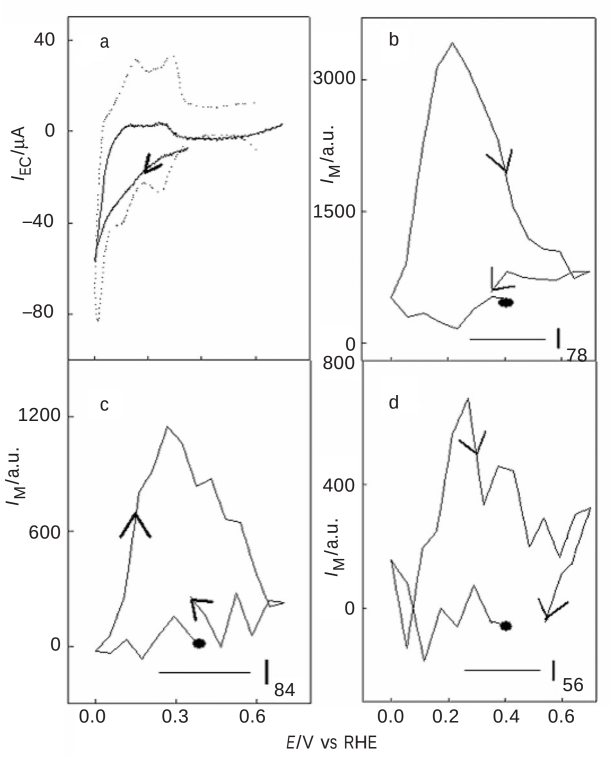


FIG. 4
Cathodic desorption of FB in 0.5 M H_2SO_4 on Pt-pc electrode, E_{ad} = 0.4 V vs RHE, cathodic switching potential 0 V, anodic switching potential 0.7 V, scan rate 20 mV s^{-1}, potential step 2 mV. a CV curves of adsorbed FB (solid line) and supporting electrolyte (dotted line); b, c and d MSCV curves for *m/z* 78: benzene, *m/z* 84 and *m/z* 56: cyclohexane, ● starting potential 0.4 V, arrows indicate the direction of polarization

lution of FB. In the adsorption mode no fluorine intermediates of FB were detected, e.g., fluorocyclohexane which is formed according to Blum et al.[21]. Nevertheless, in bulk of FB we detected fluorocyclohexane after cathodic polarization and subsequent stay in cathodic polarization limit of 0 V and –0,1 V. We assume that also fluorocyclohexane was formed in adsorption regime in very limited volume and was almost immediately dehalogenated to cyclohexane. Stay in cathodic polarization limit and high concentration of FB in bulk enabled us to observe this intermediate of FB reduction.

The formation of benzene (*m/z* 78) starts at the potential 0 V with the maximum at 0.22 V. The cyclohexane fragment (*m/z* 56) had the same potential dependence as cyclohexane. Both masses start increasing at a potential of 0.05 V and reach the maximum of 0.27 V, and both are significantly represented in the spectra of cyclohexane (*m/z* 56 and 84 representing 100 and 70.5%, respectively). Therefore we conclude that cyclohexane is formed during the FB reduction.

As mentioned above, the potential was then swept in negative direction to switching potentials of –0.1, –0.17, –0.27 and –0.37 V. We observed changes not only in the peak heights I_M of *m/z* 56, 70, 78, 84 and 96 (I_{56}, I_{70}, I_{78}, I_{84} and I_{96}) but also in their potentials. The ion current I_{78} reached a maximum at lower potentials and its magnitude was decreasing in the negative direction, e.g., from –0.1 to –0.37 V. We assume that additional hydrogenation of benzene takes place at potentials more negative than 0 V. The drop of I_{78} indicates the depletion of benzene. The maxima of ion currents I_{56} and I_{84} occurred at lower potentials and their magnitudes were increasing in the negative direction. From this fact we conclude that the amount of formed cyclohexane increased. The ion currents of FB (*m/z* 70 and 96, not shown) decreased in the switching potential range between 0 and –0.17 V. By polarization towards potentials of –0.27 and –0.37 V, respectively, a signal increase in dependence on time occurred on mass signal curves. Fluorobenzene adsorbed on Pt-pc electrode desorbs (*m/z* 96) in the course of the negative scans to –0.27 or –0.37 V (Fig. 5). No fluorocyclohexane was formed during polarization in the potential range from –0.37 to 0.7 V.

It is known that commercial organic reagents FB (CB) can contain impurities, e.g., cyclohexane. According to our MS spectra and NIST database no fragment of cyclohexane (*m/z* 84) is present in spectra of both FB and CB (Fig. 1).

Electrochemical Behavior of Chlorobenzene on Polycrystalline Platinum Electrode

Similarly to FB, CB was not only oxidized to CO_2, CB desorption was accompanied by simultaneous hydrogenation and one of the hydrogenated products was benzene. Contrary to fluorobenzene it was found that: (i) CB did not show desorption in the form of the maximum and minimum of ion currents on the measured current–time curves (time dependences of ion current I_M), (ii) CB was hydrogenated to halo derivatives, which were detected by ion current at *m/z* 67: chlorocyclohexane and *m/z* 81: 1-chlorocyclohex-1-ene.

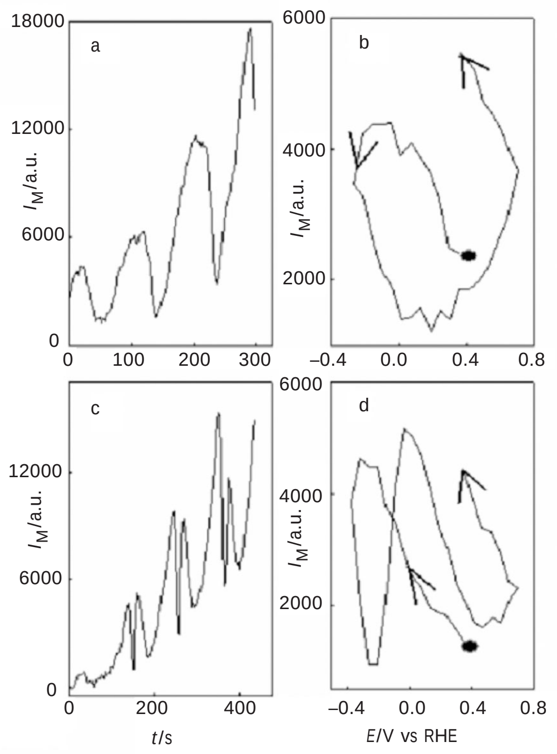


Fig. 5

Dependence of FB desorption on cathodic potential –0.27 V (a, b) and –0.37 V (c, d). a, c Mass current transient for *m/z* 96, $I_M = f(t)$ and b, d ion current for *m/z* 96, $I_M = f(E)$, ● starting potential 0.4 V, arrows indicate the direction of polarization. For other conditions see Fig. 4

Figure 6 shows direct oxidation of CB adsorbed on Pt-pc electrode. There is observed one broad oxidation peak on the CV curve with a maximum at 1.43 V situated more in the positive direction than the benzene maximum (1.35 V)[4] but at a more negative value than the maximum of FB (Fig. 2). The oxidation of CB was completed within four anodic cycles, i.e., neither CB nor FB is directly oxidized to CO_2 in contrast to benzene. Chlorobenzene starts being desorbed without oxidation at potentials where the oxide layers are formed.

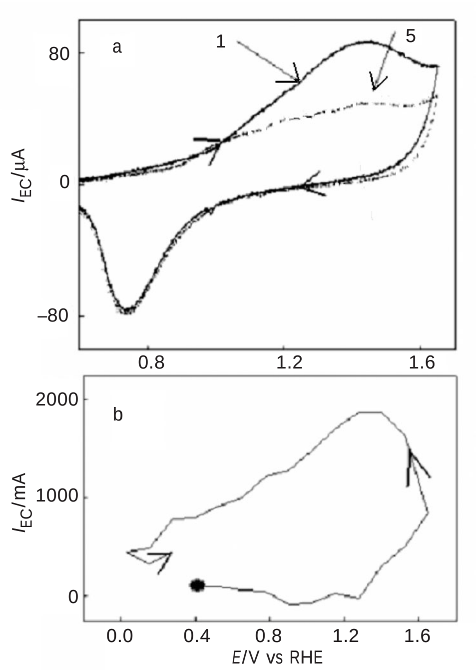


FIG. 6

a Direct oxidation of adsorbed CB in 0.5 M H_2SO_4 on Pt-pc electrode, E_{ad} = 0.4 V vs RHE, scan rate 20 mV s^{-1}, potential step 2 mV, starting potential 0.4 V, cathodic switching potential 0 V, anodic switching potential 1.62 V; the numbers 1, 5 indicate the number of cycles. b Corresponding MSCV curve for m/z 44, ● starting potential 0.4 V, arrows indicate the direction of polarization

Desorption and hydrogenation of adsorbed CB was observed in an increasing potential ranges. The cathodic switching potential was 0 V, then –0.1, –0.17, –0.27 and –0.37 V, with the unchanged anodic switching potential (0.7 V).

When the potential was first varied in the negative direction towards 0 V, we indicated potential-dependent values of ion currents I_M of *m/z* 51, 52, 53, 54, 67, 78, 79, 80, 81, 82, 83, 88, 112, 113, 114 and 116.

It was found that CB was desorbed as 1-chlorocyclohex-1-ene (*m/z* 81), chlorocyclohexane (*m/z* 67) and benzene (*m/z* 78). Formation of 1-chlorocyclohex-1-ene (*m/z* 81) starts at a potential of 0.23 V with the maximum at 0.11 V. Ion currents I_{51}, I_{53}, I_{88}, I_{116} and I_{96} showed the same potential dependence as I_{81}, and they are also represented in the spectra of 1-chlorocyclohex-1-ene (*m/z* 81, 51, 53 and 116 as 100, 17, 32 and 23%, respectively). Formation of chlorocyclohexane (*m/z* 67) starts at 0.4 V with the maximum at 0.23 V. Ion currents I_{82} and I_{83} show the same potential dependence as I_{67} (the relevant masses in the spectrum of chlorocyclohexane are: *m/z* 67, 82 and 83 representing 100, 56 and 21%, respectively). The desorption of benzene (*m/z* 78) after separation of chlorine starts at a potential of 0.24 V with the maximum at 0.11 V. The same potential dependence is also observed at ion current of masses *m/z* 79 (in the spectra of benzene as 6.5%). We noticed that during the electrochemical reduction there was an increase in ion current I_{112}, I_{113} and I_{114} with the maximum at 0.11 V, which indicates desorption of CB in the hydrogenation region.

By scanning in the region of more negative potentials at –0.1 and –0.17 V, desorption of chlorobenzene (*m/z* 112, 113 and 114), hydrogenation to chlorocyclohexane (*m/z* 67, 82, 83, 54 and 53), benzene (*m/z* 78 and 79), cyclohexa-1,3-diene and hexa-1,4-diene (*m/z* 78 amounted in these spectra to 59 and 41%, *m/z* 79 to 100% and *m/z* 80 corresponded to 76 and 60%) were detected. The volume of its hydrogenated products increased and the corresponding ion currents reached maxima at lower potentials.

Chlorobenzene adsorbed on Pt-pc electrode desorbs as cyclohexene (*m/z* 67) and also as fully hydrogenated cyclohexane (*m/z* 56) during the negative sweep to the potential limit –0.27 V (Fig. 7). In the polarization to sufficiently negative potentials the formation of cyclohexane (*m/z* 56) starts at a potential of 0.3 V with the current maximum at –0.022 V. Ion currents I_{27}, I_{29} and I_{55} showed the same potential dependence as I_{56} (the corresponding masses in the spectrum of cyclohexane are: *m/z* 56, 55, 27 and 29 with 100, 36, 37 and 13%, respectively).

As can be seen from previous observations, the choice of a negative limit of the cathodic potential is fundamental for the formation of different hydrogenation products. At a relatively positive cathodic limit of 0 V, chlorinated hydrogenation products of CB are formed 1-chlorocyclohex-1-ene, chlorocyclohexane and benzene. At a sufficiently negative potential of –0,27 V, more hydrogenated products are formed – cyclohexene and cyclohexane, while benzene and cyclohexa-1,3-diene and/or cyclohexa-1,4-diene amounts are decreasing. Chlorobenzene is desorbed in a higher amount and its maximum is shifted to the region of more negative potentials.

Comparison of Electrochemical Behavior of Fluorobenzene, Chlorobenzene and Benzene on Polycrystalline Platinum Electrode

As can be seen from previous observations, the adsorbed benzene, fluorobenzene (Scheme 1) and chlorobenzene (Scheme 2) in 0.5 M H_2SO_4 were oxidized and reduced at sufficiently positive and negative switching potentials. We observed that the adsorbed benzene was completely oxidized to the final product CO_2 already in the first cycle. The oxidation of adsorbed halogen species required a greater amount of cycles in contrast to benzene. We assume that in the particular cycles except for benzene oxidation inter-

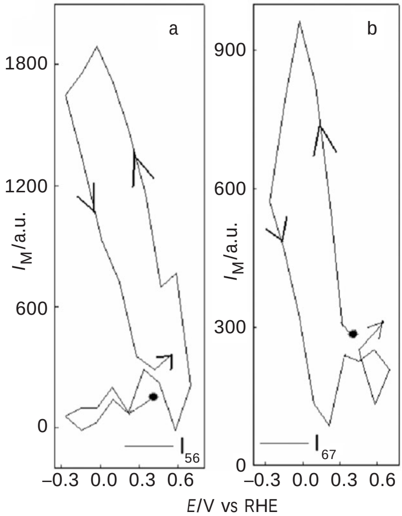
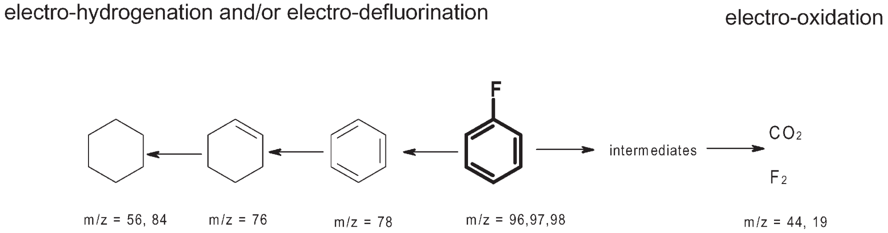


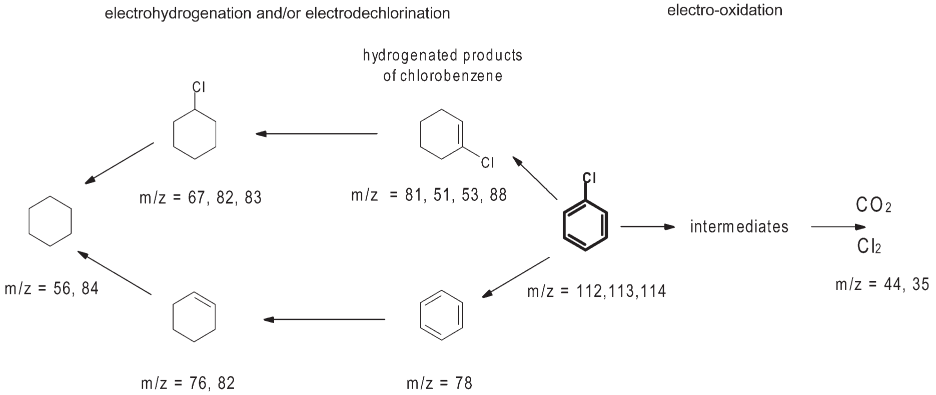
FIG. 7
MSCV curves for *m/z* 56: cyclohexane (a) and *m/z* 67: cyclohexene (b). Cathodic switching potential –0.27 V. For other conditions, see Fig 4

mediates were formed first. Benzene was already oxidized in the first cycle at the potential E_{ox} = 1.35 V. Chlorobenzene was oxidized at 1.43 V in 3 cycles and fluorobenzene at 1.47 V even in the fourth cycle. Regarding the fact that the oxidation potential E_{ox} predicts the energy of the oxidation process, we can claim that the energy necessary for the oxidation increases in the order benzene < CB < FB. This order corresponds with the number of cycles.



SCHEME 1
Electrochemical hydrogenation–oxidation of FB on Pt-pc electrode in 0.5 M H_2SO_4

Cathodic stripping of FB and CB adsorbates produces an irreversible interaction of FB and CB with platinum with the formation of adsorbed benzene and cyclohexane in the case of FB and 1-chlorocyclohex-1-ene, chlorocyclohexane, benzene, cyclohexene and cyclohexane in the case of CB. The choice of the limit potential of cathodic polarization is fundamental for the formation of different hydrogenation products.



SCHEME 2
Electrochemical hydrogenation–oxidation of CB on Pt-pc electrode in 0.5 M H_2SO_4

The adsorbed FB desorbs (*m/z* 96) in the negative scans to cathodic limits of –0.27 and –0.37 V and the adsorbed CB desorbs (*m/z* 112) in the negative sweeps to cathodic limits of 0 V.

Fluorobenzene undergoes hydrogenation more easily than chlorobenzene. The negative limit 0 V is sufficient for full hydrogenation of FB leading to cyclohexane; in the case of CB the cathodic limit should be up to –0.27 V. Moreover, for CB, higher amounts of partially hydrogenated hydrocarbons are detected. While in the case of CB partially hydrogenated chloro compounds (1-chlorocyclohex-1-ene and chlorocyclohexane) were detected, partially hydrogenated fluorocompounds were not observed.

The hydrogenation reduction potential and the corresponding energy of the reduction of benzene and the halocompounds to cyclohexane increased in the order FB < CB < benzene. Benzene was reduced at E_{red} = –0.25 V, CB at –0.02 V and FB at 0.27 V.

CONCLUSIONS

The electrochemical reactivity of FB and CB on Pt-pc electrode has not yet been investigated electrochemically in combination with mass spectrometry. The DEMS method makes it possible to detect particular hydrogenation and oxidation products and intermediates of the halocompounds in dependence on the potential. This method is restricted not only to aromatic and halogenated compounds; it is, however, convenient if the polarity of the studied compounds guarantees fluent transfer through the membrane to the MS device.

The obtained information on intermediates and products can be useful for preparation of hydrogenated compounds from halogenated aromatics at selected potentials. Moreover, despite the energy requirement the electrochemical degradation of halogenated benzene derivatives and similar compounds favors the environment because the final products of oxidation and reduction are much less toxic (CO_2, cyclohexane).

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