Electroreduction of Organic Compounds, 36 [1]. Electroreduction of Chlorinated Methyl Benzoates

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The preparative electroreduction of the three methyl monochlorobenzoates, the six methyl dichlorobenzoates, and methyl 2,3,4-trichlorobenzoate in different solvent-supporting electrolytes (SSE) was studied. The rate of the dechlorination, which is the main reaction, is dependent on the substitution pattern. Pronounced regioselectivity is therefore observed in case of the oligochloro derivatives. Hydrogenation of the benzene ring and reduction of the methoxycarbonyl group with formation of a hydroxymethyl group are observed as side-reactions. Quantum chemical calculations on the reaction mechanism were performed. The theoretical results are in accordance with the experimental observations.

Key words: Cathodic Reduction, Methyl Chlorobenzoates, Polarography, Cyclovoltammetry, Quantum Chemical Calculations

Introduction

In the past, we have studied the electrochemical dehalogenation of various types of chlorinated aliphatic [2] and, in particular, aromatic [3, 4] organic compounds. These investigations were chiefly aimed at the practical problem of degradation of hazardous polychlorinated substances which, in principle, has turned out to be feasible with electroreductive methods [4].

Although chlorinated benzoates occur in the environment [5] they are not as important and dangerous hazards as *e. g.* polychlorinated phenols, biphenyls (PCB) or dibenzodioxins. We were however, none the less, interested in their electrochemical behavior from a general point of view [6]. The strongly electron-withdrawing alkoxycarbonyl substituent should significantly influence the reducibility of the compounds. In particular, the regioselectivity of the hydrodechlorination reaction should be different as compared with the results found for chloroarenes with electron-donating substituents. Furthermore, the ester group itself could be reduced or the aromatic ring could be hydrogenated on account of the low electron density. We have therefore prepared all possible methyl monochloro-, and dichlorobenzoates as well as methyl 2,3,4-trichlorobenzoate and comprehensively studied their electrochemical behavior by voltammetric measurements and preparative electrolyses.

In order to achieve a better understanding of the course of the electrochemical reactions and of the observed selectivities, we have also performed quantum chemical calculations.

Results and Discussion

Electroanalytical results

The reduction (peak) potentials E_p of the esters **1** – **10** and methyl benzoate **11** are compiled in Table 1. They were measured by use of the differential pulse polarographic (DPP) method with an internal Ag wire as reference electrode which corresponds to the Ag/AgBr couple in the bromide containing electrolyte DMF [7]. The potentials are not converted into potentials *vs.* the SCE because we have used different and varying solvents for the preparative scale electrolyses, which would require solvent corrections to get comparable potentials.

Cyclovoltammetric measurements have revealed that only one of the observed reduction waves is reversible. This wave is found between -1.67 and -1.70 V for all compounds studied and belongs to a single electron transfer (SET) step. This SET step

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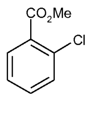
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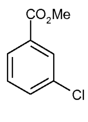
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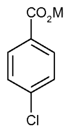
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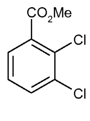
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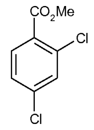
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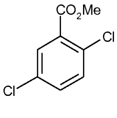
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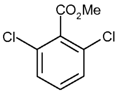
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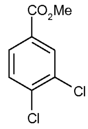
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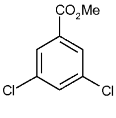
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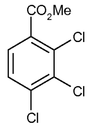
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Table 1. Polarographic (DPP) reduction potentials E_p of methyl chlorobenzoates[a,b].

Compound	E_p (V)					
11	*−1.680*	–	–	–	–	–
1	−1.295	*−1.665*	–	–	–	–
2	−1.370	*−1.675*	−1.990[c]	–	–	–
3	−1.320	*−1.680*	−1.950[c]	−2.170[c]	–	–
4	−1.100	−1.375	*−1.665*	−1.850[c]	−1.940[c]	–
5	−1.160	−1.320	*−1.675*	−1.840[c]	–	–
6	−1.150	−1.385	*−1.675*	−1.810[c]	−1.970	–
7	−1.320	*−1.700*	–	–	–	–
8	−1.135	−1.390	*−1.690*	−1.980	–	–
9	−1.150	−1.490	*−1.675*	−1.980	–	–
10	−0.990	−1.135	−1.410	*−1.670*	−1.870	−1.970

[a] Differential pulse polarographic (DPP) peak potentials as determined by use of a HMDE at scan rates of 10 mV s^{-1} in DMF *vs.* Ag/AgBr; [b] reversible steps in italics; [c] less pronounced steps.

can be clearly assigned to the formation of the methyl benzoate radical anion $\mathbf{11}^{\bullet-}$ (E_red = −1.680 V) which is known to be a persistent species and can thus be detected by EPR spectroscopy [8–10]. All other reduction waves belong to irreversible processes and are due to the transfer of two electrons (see Fig. 1) with concomitant elimination of a chloride anion *via* an ECEC mechanism [1, 11] as exemplified for the methyl monochlorobenzoates in Eqs. 1–4:

$$\begin{aligned}&\mathrm{Cl{-}C_6H_4{-}CO_2Me + e^- \rightarrow}\\&\quad\mathrm{[Cl{-}C_6H_4{-}CO_2Me]^{\bullet-}} \qquad \mathrm{E}\end{aligned} \tag{1}$$

$$\begin{aligned}&\mathrm{[Cl{-}C_6H_4{-}CO_2Me]^{\bullet-} \rightarrow}\\&\quad\mathrm{[C_6H_4{-}CO_2Me]^{\bullet} + Cl^-} \qquad \mathrm{C}\end{aligned} \tag{2}$$

$$\begin{aligned}&\mathrm{[C_6H_4{-}CO_2Me]^{\bullet} + e^- \rightarrow}\\&\quad\mathrm{[C_6H_4{-}CO_2Me]^-} \qquad \mathrm{E}\end{aligned} \tag{3}$$

$$\begin{aligned}&\mathrm{[C_6H_4{-}CO_2Me]^- + H^+ \rightarrow}\\&\quad\mathrm{C_6H_5{-}CO_2Me} \qquad \mathrm{C}\end{aligned} \tag{4}$$

The radical anions of chlorobenzoate esters are known to be extremely short-lived and not accessible to EPR measurements [12]. We could, however, indirectly detect the methyl 3-chlorobenzoate radical anions ($\mathbf{2}^{\bullet-}$) by rapid scan cyclovoltammetry. This isomer should represent the most persistent species according to our quantum chemical calculations (see below). Using a mercury microelectrode of 0.05 mm diameter and oscilloscopic registration we observed a quasi-reversible reduction step when the scan rate exceeded 500 Vs^{-1}. By computer simulation of the cyclovoltammogram, a rate constant k_chem of roughly 50–5000 s^{-1} could be estimated [13]. The reduction waves of the *ortho*- and *para*-isomers **1** and **3** remained irreversible even at a scan rate of 1000 V s^{-1}. These results are comparable with those found for chloroacetophenones. The reduction of *ortho*- and *para*-chloroacetophenone is irreversible whereas *meta*-chloroacetophenone exhibits a reversible step with $k_\mathrm{chem} = 10\ \mathrm{s}^{-1}$ [14].

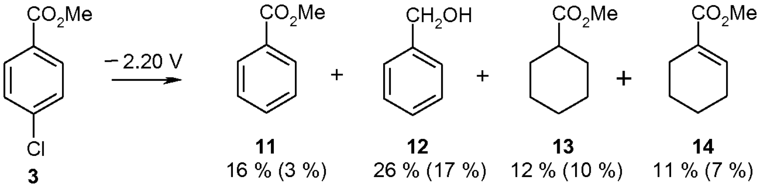
Inspection of Table 1 suggests that the successive elimination of chloride ions from the oligochloro derivatives occurs selectively. For instance, the first dechlorination step of **4** leads to a monochloro derivative with E_red = −1.375 V which agrees with E_red = −1.370 V of **2** and is thus indicative of an elimination from the 2-position of **4** – as one would expect. Similarly, E_red = −1.320 V of **5** agrees with E_red = −1.320 V of **3** but not with E_red = −1.295 V of **1** *i. e.*, the first chloride ion is split off the 2-position of **5**.

Methyl 2,6-dichlorobenzoate **7** exhibits only one single irreversible reduction step in contrast to the other derivatives. Its potential is shifted by *ca.* 150 mV into the negative direction. This effect can be explained by rotation of the ester substituent out of the arene ring plane, which is caused by steric hindrance between the two *ortho*-chloro substituents and the ester group in **7** [15]. This impedes the necessary adsorption of the substrate at the electrode surface and renders the electron transfer more difficult.

In many cases, reduction waves beyond the formation of $\mathbf{11}^{\bullet-}$ at $E_\mathrm{red} < -1.680$ V are observed. These can be assigned to further electrochemical reduction steps leading to species with a hydrogenated arene ring or functional group, which we have actually found by preparative electrolyses at low negative reduction potentials (see below).

Preparative electroreductions

Since we performed the electrolyses in the potentiostatic mode [16], exceptionally long reaction times were to be expected for experiments with complete



Scheme 1. Relative percentages of electrolysis products (21 % of recovered **3** not considered) with current efficiencies in parentheses.

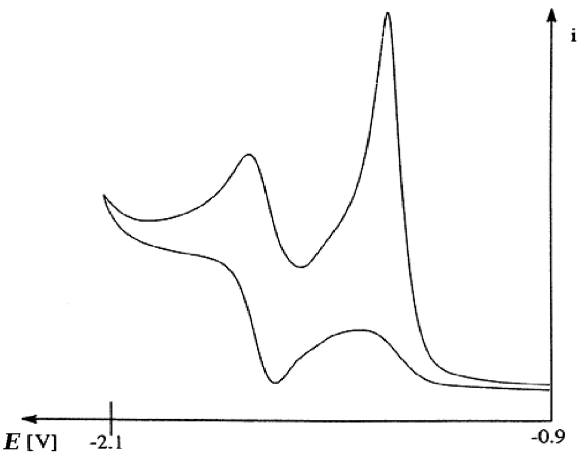


Fig. 1. Cyclovoltammogram of **1**.

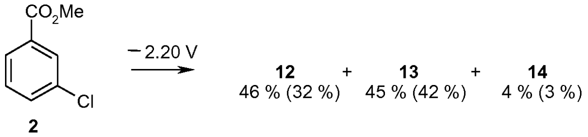
turnover. We ran the electrolyses therefore only to a certain extent and studied the reaction products irrespective of the presence of unreacted starting material. This was also meaningful for the di- and trichloro derivatives where we wanted to get insight into the selectivity of the dechlorination reaction.

When methyl *ortho*-chlorobenzoate (**1**) was electrolyzed in methanol by use of a lead cathode at $E_{\mathrm{red}} = -1.60$ V a clean dechlorination occurred to yield 73 % methyl benzoate (**11**) along with 27 % recovered **1**. A good current efficiency of 76 % was achieved. Lowering E_{red} to -1.83 V did not significantly change the result. Electroreduction at $E_{\mathrm{red}} = -2.20$ V led however to a different product mixture. Only 4 % **1** and 3 % **11** were found whereas benzyl alcohol (**12**, 60 %) and methyl cyclohexanecarboxylate (**13**, 30 %) were obtained as the predominating products. This is in agreement with L. Horner's findings on the electroreduction of ethyl benzoate. Interestingly, the chloro substituents were however retained in the products when phenyl chlorobenzoates were electroreduced, though under acidic conditions [17]. These were selectively transformed into the corresponding chlorobenzyl alcohols. This result appears to be due to the good leaving group ability of the phenoxy group and the presence of excessive protons [17].

Methyl *para*-chlorobenzoate (**3**) led to 51 % **11** besides 49 % of recovered **3** with a current efficiency of 87 % at $E_{\mathrm{red}} = -1.75$ V. No marked change was observed at $E_{\mathrm{red}} = -1.91$ V. Application of $E_{\mathrm{red}} = -2.20$ V led however to the formation of hydrogenated species as exemplified in Scheme 1.

The behavior of the *meta*-isomer **2** deviates from that of **1** and **3**. Even at $E_{\mathrm{red}} = -1.65$ V or at $E_{\mathrm{red}} = -1.76$ V considerable hydrogenation of the arene ring occurs, and 18 % methyl cyclohexene-1-carboxylate (**14**) besides 33 % of **11** and 31 % of unchanged **2** are obtained. Furthermore, the current does not drop during the course of the electrolysis as it does in the case of **1** and **3**. Instead, it remains nearly constant, which is obviously due to extensive hydrogenation of the benzene ring even at $E_{\mathrm{red}} = -1.65$ V. A selective electrochemical dechlorination of **2** is thus not possible. Presumably, the impeded electron uptake of **2** compared with **1** and **3** (*cf.* Table 1) causes hydrogenation of the arene ring before the carbon-chlorine bond is cleaved. This would lead to a chlorocyclohexenecarboxylate ester as intermediate, which is easier dechlorinated to **14** as compared with **2**. We have observed a similar effect for the cathodic dehalogenation of 2-chlorodibenzofuran, which gives 2-chloro-1,4-dihydrodibenzofuran instead of the expected dibenzofuran [18]. This effect could be rationalized by quantum chemical calculations [1], which we have also performed for **1**, **2** and **3** (see below). Expectedly, even further hydrogenation was observed at $E_{\mathrm{red}} = -2.20$ V, as shown in Scheme 2.

With a view to practical synthetic applications we have electrolyzed **1** as a model compound under varying conditions. It turned out that considerable amounts of water in the catholyte are tolerated, and even the use of aqueous sodium hydroxide solution as anolyte



Scheme 2. Relative percentages of electrolysis products (5 % of recovered **2** not considered) with current efficiencies in parentheses.

Table 2. Results of the electroreduction of **1** at $E_{\text{red}} = -1.70$ V in water-containing solvents.

Entry	Catholyte[a] MeOH/H_2O	Anolyte[a, b]	Ratio **1** : **11**	Yield[c] (%)	Current yield (%)
1	9 : 1	9 : 1	42 : 52	69	100
2	8 : 2	8 : 2	53 : 47	68	83
3	7 : 3	7 : 3	58 : 42	35	72
4	9 : 1	H_2O	50 : 50	77	100
5	MeOH	H_2O, NaOH	59 : 41	69	100
6	9 : 1	H_2O, NaOH	70 : 30	66	99
7	8 : 2	H_2O, NaOH	28 : 72	53	100
8	7 : 3	H_2O, NaOH	57 : 43	77	82

[a] Tetraethylammonium bromide (TEAB) as supporting electrolyte if not stated otherwise; [b] MeOH/H_2O as solvent if not stated otherwise; [c] sum of isolated material (**1** + **11**).

Table 3. Results of the electroreduction of the methyl oligochlorobenzoates **4** – **10** in methanol as catholyte and aqueous NaOH as anolyte.

Compound	E_{red} (V)	Turnover (%)	Products (%)					
			2	**3**	**1**	**11**	**8**	**4**
4	−1.45	60	100					
5	−1.40	35		98	1			
6	−1.40	41	100					
7	−1.50	74			98	2		
8	−1.42	62	100					
9	−1.45	45	100					
10	−1.30	80					90	2[a]

[a] Plus 8 – 9 % unidentified products.

allows one to achieve reasonable dechlorination rates. These results are compiled in Table 2. The use of sodium hydroxide instead of TEAB as supporting electrolyte in the anodic compartment of the cell offers an important advantage since oxygen is now the anodic product while bromine results from TEAB. Furthermore, the conductance is higher and consequently the cell voltage can be significantly lower, which we have especially observed when the electrode potential was kept at $E_{\text{red}} = -2.20$ V.

The electroreduction of the di- and trichlorobenzoate esters was carried out at low cathode reduction potentials in order to detect the primary products. Since this causes low current densities and very long reaction times, the electrolyses were finished at turnover rates of 80 % at most. In accordance with the results on the three monochlorobenzoate isomers, the cathodic reduction of all methyl dichlorobenzoates, which carry one of the chloro substituents in the 3-position (**4**, **6**, **8** and **9**), leads to methyl 3-chlorobenzoate (**2**) as the predominating primary product (see Table 3).

While this is of course trivial for the 3,5-isomer **9**, the striking selectivity found also for **4**, **6** and **8** is again indicative of the specific impediment to splitting of the C-3–Cl bond. Also, the splitting of a C-2–Cl bond of **5** and of the trichlorobenzoate ester **10** is nearly exclusively favored compared with the splitting of a C-4–Cl bond.

Table 4. Charges and electron densities in the SOMOs of methyl chlorobenzoates.

Radical anion	Charge at the Cl atom	SOMO-Electron density at the Cl atom
$\mathbf{1}^{\bullet-}$	−0.092	−0.083
$\mathbf{2}^{\bullet-}$	−0.093	−0.043
$\mathbf{3}^{\bullet-}$	−0.111	−0.108

The outcome of the preparative electrolyses of the monochlorobenzoate esters on the one hand is thus in perfect agreement with that of the di- and trichlorobenzoate esters on the other hand, and the results are also in accordance with the electroanalytical data. One can state the following order for the reducibility of the C–Cl bonds of methyl oligochlorobenzoates:

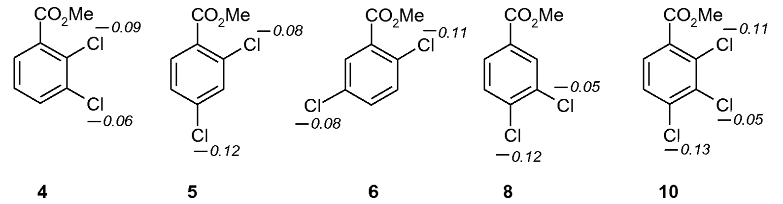
$$ortho > para \gg meta$$

in agreement with Bartak's results on chloroacetophenones [14] and the findings of Andrieux and Savéant [19] on various haloarenes, but in contrast to the order *meta* ≈ *para* > *ortho* observed for the dechlorination of oligochlorotoluenes, and *meta* > *ortho* > *para* in the oligochloroanisole series [3].

Quantum chemical calculations

In order to achieve a better understanding and find out the reasons of the observed effects, we have performed semi-empirical AM1-type [20] quantum chemical calculations. First, the electron and charge density distributions of the radical anions $\mathbf{1}^{\bullet-}$, $\mathbf{2}^{\bullet-}$ and $\mathbf{3}^{\bullet-}$ were calculated. Table 4 shows the relevant figures.

Inspection of the results shows that one cannot predict the different reactivities of the three isomers merely from the charge densities, although, in accordance with the experiments, the electron density at the chloro substituent is actually the lowest in the *meta*-position ($\mathbf{2}^{\bullet-}$). Rather, it was necessary to take a look on the bond breaking step. We have therefore calculated the reaction paths for the dechlorination process. The length of the C–Cl bond was used as the reaction coordinate, and the bond angle was not fixed but optimized during the calculation. Solvent effects were taken into account by use of the COSMO (COnductor like Screening MOdel) method [21]. The reaction paths of the three isomers are shown in Fig. 2.



Scheme 3. SOMO electron densities in the radical anions **4**$^{\bullet-}$, **5**$^{\bullet-}$, **6**$^{\bullet-}$, **8**$^{\bullet-}$, and **10**$^{\bullet-}$.

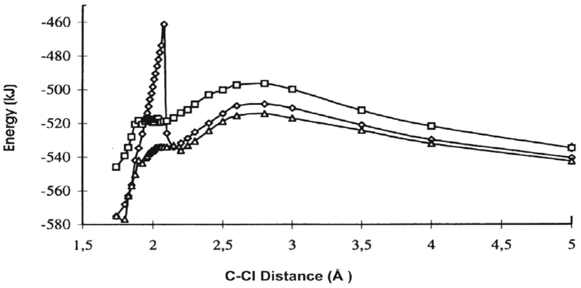


Fig. 2. Reaction coordinates for the electroreductive dechlorination of **1** (–□–), **2** (–◇–) and **3** (–△–).

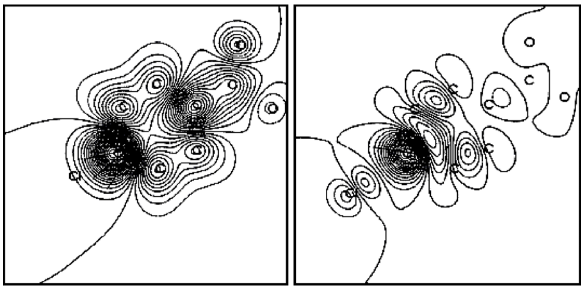


Fig. 3. Intersections through the SOMO of **3**$^{\bullet-}$ at 0.7 Å above the plane of the benzene ring [left: at the beginning of the reaction path; right: at nearly complete splitting of the C–Cl bond ($d_{\text{C–Cl}}$ = 2.8 Å)].

One recognizes the unusually high activation energy for the dechlorination step of the *meta*-isomer **2**. This step is obviously impeded. The calculated reaction path thus reflects the anomalous behavior of **2**.

Our calculations also have revealed that during the elongation of the C–Cl bond the charge transfer mainly occurs at a distance between 1.9 – 2.1 Å ending up with the final formation of a free chloride ion. Furthermore, prior to the bond breaking the π-SOMO is transformed into a σ-SOMO, which is mainly localized at the C–Cl bond, *cf.* Fig. 3.

This finding agrees with Casado's [22], Pierini's [23] and Andrieux's [19] theoretical results on chlorobenzene and other haloarenes. More recently, Pierini *et al.* performed *ab initio* (DFT-B3LYP) MO calculations on the radical anions of chloroacetophenones in the gas phase as well as in polar solvents, which is obviously important at least for the final formation of the free chloride anion [24]. Their results agree with the experimentally observed reactivities. The order of the rate constants for the dechlorination was found to be *meta*-chloroacetophenone < *para*-chloroacetophenone. Unfortunately, the behavior of the *ortho*-isomer was not taken into consideration. The beginning of the splitting step is rather well reproduced, and a local minimum is observed for the σ-SOMO which is formed at a C–Cl distance of 1.99 – 2.11 Å. The same is true for our results. A marked energy minimum between 2.0 and 2.2 Å occurs for the *meta*-isomer **2** whereas **1** and **3** exhibit only weak local minima. Hence, the charge transfer occurring at 1.9 – 2.1 Å can be explained with the re-hybridization of the SOMO. This rehybridization is responsible for the dissociation of the radical anion because the σ-SOMO is localized at the C–Cl bond.

Fontanesi *et al.* [25] have tried to predict the successive chloride eliminations of chlorinated benzenes from the electron densities in the SOMOs, which attempt was however only partially successful. We have also tried to correlate the selectivity of the dechlorination of the asymmetrically substituted methyl dichlorobenzoates **4**, **5**, **6**, **8**, and methyl trichlorobenzoate **10** with the SOMO electron densities (see Scheme 3). The numbers at the chlorine substituents in Scheme 3 represent the SOMO electron densities as calculated by the AM1 method.

The experimentally observed retarded elimination of a chloro substituent from the *meta*-position of the esters is well reproduced by the lowest calculated SOMO electron densities at C-3. Since an intramolecular electron transfer occurs during the bond breaking, a highest possible electron density of the chlorine atom at the beginning of the process is favorable. However, the difference between the *ortho*- and the *para*-position cannot be correctly predicted as the figures for **5** and **10** show. Even an inclusion of the solvent effect into the calculations [26] does not improve this result.

As we had achieved more convincing results with calculations of the reaction paths in the monochloro-

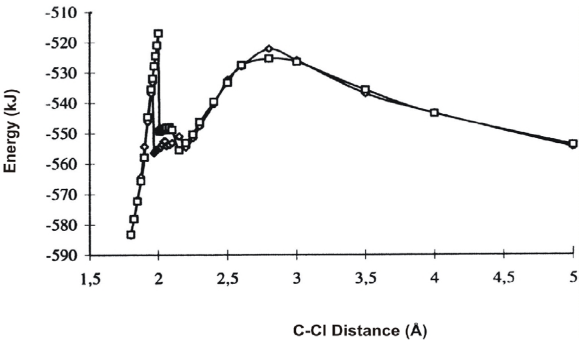


Fig. 4. Energy of the radical anion $5^{\bullet-}$ in dependence of the C–Cl bond lengths (*ortho*: –◇–, *para*: –□–).

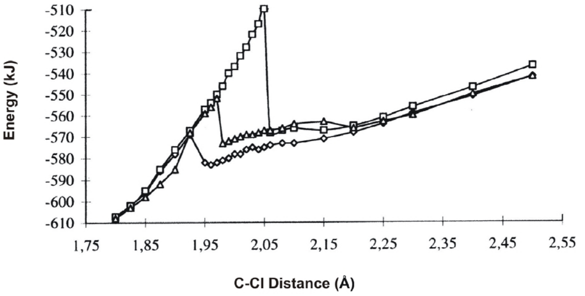


Fig. 5. Energy of the radical anion $10^{\bullet-}$ in dependence of the C–Cl bond lengths (*ortho*: –◇–, *meta*: –□–, *para*: –△–).

benzoate series we have also performed corresponding calculations for **5** and **10**. The reaction coordinates are shown in Figs. 4 and 5.

Obviously, the deciding step concerning the regioselectivity of the reaction is, once more, the transformation of the π radical anion into a σ radical anion. For both $5^{\bullet-}$ and $10^{\bullet-}$ the activation energy of the $\pi \rightarrow \sigma$ transition for the chloro substituent in the *para*-position is higher than in the *ortho*-position. The activation energy for the *meta*-position in $10^{\bullet-}$ is significantly higher as compared with the *ortho*- or *para*-position. This effect causes the pronounced regioselectivity in favor of the chloride elimination from the *ortho*- and *para*-positions, which is observed during the preparative electroreduction of **10**, whereas the difference between the latter two positions is less significant. The results are compiled in Table 5.

Conclusion

Methyl *ortho*- and *para*-chlorobenzoate (**1** and **3**) are cleanly transformed into methyl benzoate (**12**) by potentiostatic electroreduction in methanol whereas the *meta*-isomer (**2**) yields methyl cyclohexene-1-carboxylate (**14**) besides **12**. The methyl di- and trichlorobenzoates **4** – **10** are dechlorinated step by step to form selectively one single monochloro derivative as the first intermediate. Predominantly, **2** is obtained if a *meta*-chloro substituent is present in the starting compound. The electroanalytical and, in particular, the preparative results have been rationalized through semi-empirical MO (AM1-type) calculations. Electron densities or net charges in the ground states of the radical anions are only partially suitable to explain the experimental findings. However, the calculation of the reaction coordinates and of the corresponding activation energies provides correct predictions of the observed selectivities.

Table 5. Activation energies ΔH_A [kJ mol^{-1}][a] for the $\pi \rightarrow \sigma$ transition of the SOMO in $5^{\bullet-}$ and $10^{\bullet-}$.

Compound	*ortho*-chloro	*meta*-chloro	*para*-chloro
$5^{\bullet-}$	50	–	66
$10^{\bullet-}$	38	97	56

[a] The absolute figures may not be exact, but the relative order should be realistic.

Experimental Section

Melting points (corrected): Electrothermal. – NMR spectra were recorded on a WH 270 spectrometer (Bruker) at 250 MHz (^{1}H) and 62.9 MHz (^{13}C) in $CDCl_3$. IR spectra: FT-IR 1720X (Perkin-Elmer) and Genesis (ATI-Mattson). Mass spectra: CH 7 (70 eV, Varian). Analytical GC: GC 4200 (Carlo Erba) equipped with a 50 m fused silica capillary SE 54 column (Macherey & Nagel). Preparative GC: GC-8A (Shimadzu) equipped with a 3 m steel column packed with 10 % SE 30 on Chromosorb WAW and heat conductance detector. GC-MS: GC 5970 (Hewlett Packard) coupled with a mass-selective detector and equipped with a 50 m fused silica capillary SE 54 column (Macherey & Nagel). Differential pulse polarography: VA 663/Polarecord 626 (Metrohm). Cyclic voltammetry: VA-Scanner E 612 (Metrohm) with plotter Servotec 7040 A (Hewlett Packard) or Oscilloscope T 912 (Tektronix) at high sweep rates. Potentials were measured in MeOH/0.1N tetraethylammonium bromide (TEAB) or DMF/0.1N TEAB *vs.* an internal Ag wire as reference electrode, which corresponds to the Ag/AgBr couple in the TEAB solution [7].

Starting compounds

The chlorinated benzoic acids except 2,3,4-trichlorobenzoic acid are commercially available. The corresponding methyl esters were prepared by acid-catalyzed esterification of the respective acids with MeOH according to a standard laboratory procedure [27] if not stated otherwise (**7**). The reference ester **14** is also commercially available (Fluka).

2,3,4-Trichlorobenzonitrile

Sandmeyer reaction [27, 28] of 2,3,4-benzenediazonium chloride [prepared from 2,3,4-trichloroaniline (Fluka, 18.6 g, 0.095 mol)] with CuCl (9.9 g, 0.10 mol) and NaCN (13.0 g, 0.26 mol) gave 2,3,4-trichlorobenzonitrile (7.3 g, 37 %). – M. p. 93 – 94 °C. (lit. [29]: 87 °C). – IR (KBr): ν = 2235 (C≡N) cm^{-1}. – ^{1}H NMR: δ = 7.48 – 7.57 (dd, AB system, $J_{5,6}$ = 8 Hz, 2 H, 5-H, 6-H). – ^{13}C NMR: δ = 113.5 (C-1), 114.9 (CN), 128.4 (C-3), 129.0 (C-5), 131.5 (C-6), 133.8 (C-2), 137.2 (C-4).

2,3,4-Trichlorobenzoic acid

2,3,4-Trichlorobenzonitrile (5.0 g, 0.024 mol) was refluxed with H_2SO_4 (68 mL, 75 %) for 5 h. The acid was precipitated by addition of H_2O and purified by column chromatograpy. Yield: 0.4 g (7 %). – M. p. 187 °C. (lit. [30]: 192 – 194 °C). – ^{1}H NMR: δ = 7.50 (d, $J_{5,6}$ = 8 Hz, 1 H, 6-H), 7.82 (d, $J_{5,6}$ = 8 Hz, 1 H, 5-H).

*Methyl 2-chlorobenzoate (**1**)*

1 was obtained from 2-chlorobenzoic acid (39.1 g, 0.25 mol). Yield: 36.6 g (86 %). – B. p. 108 °C/30 Torr (lit. [31]: 229 – 230 °C, lit. [32]: 119.5 – 120.5 °C/24.4 Torr). – IR (film): ν = 1735 (C=O) cm^{-1}. – ^{1}H NMR: δ = 3.90 (s, 3 H, *Me*), 7.24 – 7.83 (m, 4 H, ArH).

*Methyl 3-chlorobenzoate (**2**)*

2 was obtained from 3-chlorobenzoic acid (39.1 g, 0.25 mol). Yield: 34.9 g (82 %). – B. p. 110 °C/30 Torr (lit. [31]: 114 °C/18 Torr). – IR (film): ν = 1735 (C=O) cm^{-1}. – ^{1}H NMR: δ = 3.92 (s, 3 H, *Me*), 7.31 – 8.10 (m, 4 H, ArH).

*Methyl 4-chlorobenzoate (**3**)*

3 was obtained from 4-chlorobenzoic acid (39.1 g, 0.25 mol). Yield: 38.8 g (91 %). – M. p. 41 – 43 °C (lit. [31]: 43 – 43.5 °C). – IR (KBr): ν = 1723 (C=O) cm^{-1}. – ^{1}H NMR: δ = 3.92 (s, 3 H, *Me*), 7.40 (m, 2 H, 3/5-H), 7.97 (m, 2 H, 2/6-H).

*Methyl 2,3-dichlorobenzoate (**4**)*

4 was obtained from 2,3-dichlorobenzoic acid (1.2 g, 0.006 mol). Yield: 0.67 g (52 %). – M. p. 36 °C. – IR (KBr): ν = 1723 (C=O) cm^{-1}. – ^{1}H NMR: δ = 3.95 (s, 3 H, *Me*), 7.26 (t, $J_{4,5}$ = $J_{5,6}$ = 8 Hz, 1 H, 5-H), 7.60 (dd, $J_{4,6}$ = 1 Hz, $J_{5,6}$ = 8 Hz, 1 H, 4-H), 7.68 (dd, $J_{4,6}$ = 1 Hz, $J_{5,6}$ = 8 Hz, 1 H, 6-H), in agreement with lit. [33].

*Methyl 2,4-dichlorobenzoate (**5**)* [34]

5 was obtained from 2,4-dichlorobenzoic acid (9.0 g, 0.041 mol). Yield: 8.5 g (88 %). – B. p., lit. [34]: 132 °C/15 Torr. – IR (KBr): ν = 1737 (C=O) cm^{-1}. – ^{1}H NMR: δ = 3.94 (s, 3 H, *Me*), 7.22 (dd, $J_{3,5}$ = 2 Hz, $J_{5,6}$ = 8 Hz, 1 H, 5-H), 7.40 (d, $J_{3,5}$ = 2 Hz, 1 H, 3-H), 7.72 (d, $J_{5,6}$ = 8.2 Hz, 1 H, 6-H).

*Methyl 2,5-dichlorobenzoate (**6**)*

6 was obtained from 2,5-dichlorobenzoic acid (7.0 g, 0.037 mol). Yield: 5.5 g (73 %). – M. p. 38 °C. (lit. [35]: 38 °C). – IR (KBr): ν = 1731 (C=O) cm^{-1}. – ^{1}H NMR: δ = 3.92 (s, 3 H, *Me*), 7.40 (m, 2 H, 3-H, 4-H), 7.82 (m, 1H, 6-H). – ^{13}C NMR: δ = 52.7 (*Me*), 131.1 (C-1), 131.3 (C-3), 132.14 (C-5), 132.3 (C-6), 135.2 (C-2), 132.6 (C-4), 164.9 (C=O).

*Methyl 2,6-dichlorobenzoate (**7**)*

2,6-Dichlorobenzoic acid (2.0 g, 0.010 mol), $NaHCO_3$ (1.8 g, 0.025 mol) and Na_2SO_4 (1 g) were dissolved in dry DMF (30 mL). Iodomethane (2.0 mL, mol) was dropped into the solution under cooling with ice. The reaction mixture was stirred at 20 °C for 20 h, subsequently shaken with an aqueous $Na_2S_2O_3$ solution (30 mL) and extracted with diethyl ether. The extract was dried over $MgSO_4$. The solvent was removed and the residue chromatographed on SiO_2. Yield: 1.5 g (70 %). – M. p. 26 °C (lit. [36]: B. p. 250 °C, [37]). – IR (KBr): ν = 1708 (C=O) cm^{-1}. – ^{1}H NMR: δ = 3.96 (s, 3 H, *Me*), 7.25 – 7.35 (m, 3 H, 3/4/5-H). – ^{13}C NMR: δ = 53.0 (*Me*), 127.8 (C-3/5), 131.0 (C-4), 131.9 (C-2/63), 133.5 (C-1), 165.3 (C=O).

*Methyl 3,4-dichlorobenzoate (**8**)*

8 was obtained from 3,4-dichlorobenzoic acid (11.3 g, 0.059 mol). Yield: 10.4 g (79 %). – M. p. 47 °C (lit. [38]: 45 – 47 °C). – IR (KBr): ν = 1733 (C=O) cm^{-1}. – ^{1}H NMR: δ = 3.94 (s, 3 H, *Me*), 7.53 (d, $J_{5,6}$ = 8.1 Hz, 1 H, 5-H), 7.84 – 7.89 (dd, $J_{2,6}$ = 2 Hz, $J_{5,6}$ = 8.1 Hz, 1 H, 6-H), 8.12 (d, $J_{2,6}$ = 2 Hz, 1 H, 2-H). – ^{13}C NMR: δ = 52.6 (*Me*), 128.6 (C-5), 129.9 (C-1), 130.5 (C-2), 131.5 (C-6), 132.9 (C-3), 137.6 (C-4), 165.2 (C=O).

*Methyl 3,5-dichlorobenzoate (**9**)*

9 was obtained from 3,5-dichlorobenzoic acid (4.0 g, 0.021 mol). Yield: 2.7 g (63 %). – M. p. 58 °C (lit. [39]: 58 °C). – IR (KBr): ν = 1734 (C=O) cm^{-1}. – ^{1}H NMR: δ = 3.94 (s, 3 H, *Me*), 7.54 (m, 1 H, 4-H), 7.90 (m, 2 H, 6-H). – ^{13}C NMR: δ = 52.6 (*Me*), 127.9 (C-2/6), 132.6 (C-4), 132.7 (C-1), 135.1 (C-3/5), 164.6 (C=O). – MS: *m/z* (%) = 208 (2), 206 (16), 204 (27) $[M]^+$, 177 (9), 175 (61), 173 (100) $[M - OCH_3]^+$, 147 (28), 145 (44) $[M - CO_2CH_3]^+$, 111 (14), 109 (35), 76 (47), 74 (58), 50 (19).

*Methyl 2,3,4-trichlorobenzoate (**10**)*

10 was obtained from 2,3,4-trichlorobenzoic acid (0.40 g, 0.0018 mol). Yield: 0.40 g (94 %). – M. p. 63 – 65 °C (lit. [30]: 63 – 66 °C). – IR (KBr): ν = 1738 (C=O) cm^{-1}. – ^{1}H NMR: δ = 3.95 (s, 3 H, *Me*), 7.45 (d, $J_{5,6}$ = 8 Hz, 1 H, 5-H), 7.63 (d, $J_{5,6}$ = 8 Hz, 1 H, 6-H), in agreement with lit. [30].

Preparative electroreductions

The electrolyses as performed by use of a divided batch cell and the work-up procedure have been described elsewhere [3]. The identification of the products as dealt with in the text, in Scheme 2 and 3, and in Table 2 and 3 was achieved by GC *via* co-injection of authentic reference compounds.

Quantum chemical calculations

IBM-RS 6000, VAX III, Siemens S 100 and Convex 120 computers were used for the calculations. Starting geometries were calculated by use of force field methods (program SYBYL). Semi-empirical AM1-type [20, 40] MO calculations were performed by use of the QCPE program packages MOPAC 6.0 and MOPAC 93 [41]. Closed-shell molecules were calculated with the RHF method. Open-shell systems (radical anions) were calculated with CI-methods. The QCPE programs DRAW and DENSITY were used for the graphical presentation of the results.

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