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Electrocarboxylation of CCl_4 in MeCN during electrolysis with the sacrificial Zn anode*

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The regularities of galvanostatic electrocarboxylation of CCl_4 in Alk_4NBr/MeCN in an undivided cell with sacrificial Zn anode were studied. The major product of the electrolysis is zinc trichloroacetate, which is formed as a result of the reaction of the cathode-generated CCl_3^- anion with CO_2. The further trichloroacetate reduction is prevented by cathode passivation. Therefore, small amounts of zinc dichloro- and monochloroacetates are formed due to the chemical reduction of zinc trichloroacetate with Zn^0 rather than the cathodic reduction. Zero-valence zinc is formed in minor amounts when Zn^{2+} ions are discharged at the cathode surface because of the low solubility of $ZnBr_2$ in MeCN. The treatment of $(Cl_3CCOO)_2Zn$ with H_2SO_4 in MeOH gives Cl_3CCO_2Me in 11% yield based on the starting CCl_4.

Key words: electrochemical carboxylation, sacrificial zinc anode, tetrachloromethane, carbon dioxide, trichloroacetic acid.

In the previous work,[1] we studied the galvanostatic electrochemical carboxylation of CCl_4 in DMF in an undivided cell with the sacrificial Zn anode and revealed regularities of this process. The reduction of CCl_4 generating the CCl_3^- anion was found to be accompanied by reduction of Zn^{2+} salts formed thereupon with the formation of Zn^0 on the cathode. The only product of CCl_4 electrocarboxylation was zinc dichloroacetate formed due to the chemical reduction of the corresponding trichloroacetate (primary product of electrocarboxylation of CCl_4) by Zn^0 freshly precipitated on the cathode. In addition, zinc trichloro-acetate turned out to be very unstable[1] in DMF and decomposed to evolve CO_2.

It should be emphasized that a reason for the low yield of dichloroacetate (<10% based on the starting CCl_4) is[1] predomination of the destruction of zinc trichloroacetate over its chemical reduction by Zn^0. Taking into account that the competition is also observed between the reduction of Zn^{2+} salts and CCl_4 reduction that occurs only on the cathode surface unoccupied with Zn^0,[1] we may suggest that the electrocarboxylation of CCl_4 in DMF as a whole is rather complicated process affected by a combination of several opposite factors.

It follows that the choice of DMF as a medium[1] for CCl_4 electrocarboxylation was unsuccessful, although this solvent is rather often used for electrocarboxylation in systems with the sacrificial anode as, *e.g.*, in Refs 2—4. Therefore, we focused the development of works on CCl_4 electrocarboxylation first on the selection of solvent that would provide stability of zinc polychlorocarboxylates as expected products of CCl_4 electrocarboxylation. In the present work, MeCN was studied as such a solvent, which as DMF is an aprotic dipolar solvent with the dielectric constant value close to that of DMF but with lower dissociating ability.[5]

As earlier,[1] electrocarboxylation was carried out under galvanostatic undivided electrolysis of CCl_4 with the Zn anode and steel cathode, bubbling CO_2 through an electrolyte at atmospheric pressure.

Results and Discussion

The choice of MeCN as a medium for CCl_4 electrocarboxylation was reasonable, which is substantiated by the results of preliminary studies of the comparative chemical stability of the authentic[1] zinc polychloroacetate samples in DMF and MeCN. For this purpose, equimolar samples (0.005 mol) of zinc trichloro- and dichloroacetate were placed in DMF and MeCN, respectively, and the mixtures were stirred for certain time. Zinc trichloroacetate in DMF solution decomposed intensely to evolve CO_2 (see Ref. 1).

We assumed that bis(trichloromethyl)zinc formed intermediately is also unstable and decomposes further to give $ZnCl_2$ and dichlorocarbene (Scheme 1).

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Scheme 1

$$(Cl_3CCOO)_2^{-}Zn^{2+} \xrightarrow[-2CO_2]{} (Cl_3C)_2^{-}Zn^{2+} \xrightarrow[-2:CCl_2]{} ZnCl_2$$

If the proposed scheme of decomposition is correct, then, after distillation of the easily removed destruction products and DMF, the weight of the dry residue should correspond to the amount of $ZnCl_2$ formed calculated from Scheme 1. This is consistent with our experimental results. Somewhat larger values (39.6 %, Table 1) compared to the calculated ones (34.6% for dry $ZnCl_2$) are probably due to difficulties of complete DMF removal. Moreover, it is seen from the data in Table 1 that the weight of the residues after solvent was distilled off is the same in experiments with stirring of zinc trichloroacetate just in DMF for 1 and 4 h. This means that just 1 h after zinc trichloroacetate decomposes almost completely. Unlike DMF, in MeCN zinc trichloroacetate is stable, no gas release was observed upon stirring of the solution for both 1 and 4 h, and after MeCN was removed the weight of the dry residue (see Table 1) was 100% of the initial sample weight. In the case of zinc dichloroacetate, no gas release occurred in both DMF and MeCN media. In these experiments, the weight of the residues after solvent removal was equal to the weight of the initial samples, which indicates the stability of zinc dichloroacetate in the both solvents.

Based on these results, one could expect that the electrocarboxylation of CCl_4 in MeCN would be more efficient. Indeed, the composition and yield of the CCl_4 electrocarboxylation products in MeCN differ from those obtained in DMF (Table 2). For the electrocarboxylation in DMF (Table 2) the reproducibility of the results was low,[1] whereas it was good for all experiments in MeCN. For product identification, the obtained mixture of zinc salts of (poly)chloroacetic acids was transformed into a mixture of the corresponding methyl esters, which was analyzed by ^1H NMR spectroscopy.

This mixture usually consisted of methyl esters of trichloroacetic (MET), dichloroacetic (MED), and monochloroacetic (MEM) acids. It has previously[1] been shown that the CCl_4 electrocarboxylation products are formed due to both electrochemical and chemical stages of the electrode process and, hence, their current yields (especially for dichloro- and chloroacetates) are rather ambiguous. This impelled us to determine the substance yield of each (poly)chloroacetate (based on the starting CCl_4) using the ^1H NMR spectroscopic data for the corresponding mixtures. Note that in all experiments the passed electric charge (Q) was less than the theoretical value (Q_{theor}) based on the first two-electron step (see Scheme 2, *a*) and usually did not exceed 6000—7000 C because of cathode passivation.

Table 1. Relative stability of salts $(Cl_3CCOO)_2Zn$ and $(Cl_2CHCOO)_2Zn$ in DMF and MeCN

Solvent	t/h	Weight of dry residue* (% of starting weighed sample)	
		$(Cl_3CCOO)_2Zn$	$(Cl_2CHCOO)_2Zn$
DMF	1	39.6	100.0
	4	39.5	100.0
MeCN	1	100.0	100.0
	4	100.0	100.0

* The residue was obtained upon solvent removal after stirring a weighed sample of the corresponding zinc salt in the solvent for 1 or 4 h (4 h is the maximum electrolysis time).

The data in Table 2 show that the total yield of chloroacetates in electrocarboxylation increases 2.5-fold when DMF is replaced by MeCN, and not MED but MET is formed as the major product.

We believe that these results are due to both the difference in stability of zinc trichloroacetate in DMF and MeCN (see Table 1) and the presence of different amounts of freshly precipitated Zn^0 on the cathode in these solvents. The freshly precipitated Zn^0 acts as a reducing agent with respect to zinc polychloroacetates.[1]

It turned out that the electrolysis of 0.1 M Et_4NBr in DMF with Zn anode/Fe cathode system resulted in the dissolution of the Zn anode and generation of Zn^{2+} ions with 100% current efficiency. The solution remained transparent, and a black film of freshly precipitated Zn^0 appeared on the cathode surface. An analogous experiment in MeCN also resulted in the dissolution of the Zn anode with 100% current efficiency. However, in this case, the cathode surface was only partly covered with a black film , while the solution, on the contrary, rapidly became turbid and transformed into a white suspension. It can be assumed that $ZnBr_2$ formed during electrolysis is less soluble in MeCN than in DMF. This minimizes, in turn, the reduction of Zn^{2+} ions with Zn^0 formation on the cathode surface. This is the reason why the contribution of chemical reduction of zinc trichloroacetate

Table 2. Influence of the solvent nature on the composition of the electrolysis products[a] and the yield of chloroacetic esters during electrocarboxy-lation (EC) of CCl_4

Entry	Solvent	Total yield of chloroacetates/g	Composition of EC products[b] (yield (%))		
			MET	MED	MEM
1	DMF	0.46	0.0	95.3 (6.1)	4.7 (<1)
2	MeCN	1.16	77.3 (10.1)	17.0 (2.8)	5.7 (1.3)

[a] C_{CCl_4} = 0.5 mol L^{-1}, 0.1 M Et_4NBr, steel St3 cathode, anode Zn, j = 9.4 mA cm^{-2}, T = 20 °C, Q = 6900 C (71.5% of Q_{theor} based on the two-electron process).

[b] Calculated from the ^1H NMR spectral data.

Table 3. Influence of $ZnCl_2$ additives on the composition of the electrolysis products[a] upon CCl_4 electrocarboxylation (EC)

Entry	$ZnCl_2$ /mol	Solvent	Total yield of chloro-acetates/g	Composition of EC products (выход (%))		
				MET	MED	MEM
1	—	DMF	0.46	0.0	95.3 (6.1)	4.7 (<1)
2	0.015	DMF	1.0	0.0	76.0 (10.6)	24.0 (4.4)
3	—	MeCN	1.16	77.3 (10.1)	17.0 (2.8)	5.7 (1.3)
4	0.015	MeCN	0.76	41.7 (3.6)	31.2 (3.3)	27.1 (3.7)

[a] The conditions are given in Note to Table 2.

(primarily formed due to CCl_4 electrocrboxylation) to dichloroacetate by Zn^0 was lower in MeCN than in DMF (see Table 2).

After $ZnCl_2$ was added to a 0.1 *M* solution of Et_4NBr in MeCN, a black film of Zn^0 efficiently precipitated on the cathode during electrolysis. Evidently, this indicates that $ZnCl_2$ is better soluble in MeCN than $ZnBr_2$. The results of these experiments (Table 3) agree completely with the developed concepts on the effect of the solvent nature on the regularities of CCl_4 electrocarboxylation, confirming that the main role in the formation of zinc dichloroacetate from the primarily formed trichloroacetate belongs to the chemical reduction of the latter by freshly precipitated Zn^0.

Additives of $ZnCl_2$ during electrolysis in DMF increased the yield of zinc dichloroacetate (*cf.* entries *1* and *2*, Table 3) and also produced noticeable amounts of zinc monochloroacetate.

It is quite obvious that this result is due to an increase of the amount of the reducing agent Zn^0 formed on the cathode surface and an increase in the fraction of di- and monochloroacetates, respectively. For the same reason, additives of $ZnCl_2$ (which is better soluble in this medium than $ZnBr_2$) for the electrolysis in MeCN increase the yield of zinc dichloro- and especially monochloroacetate (*cf.* entries *3* and *4*) and decrease the yield of zinc trichloroacetate. Some decrease in the total yield of polychloroacetates from 1.16 g (entry *3*) to 0.76 g (entry *4*) is evidently due to a change in the ratio and, hence, the total molecular weight of the target products.

The study of factors affecting the yield and composition of the CCl_4 electrocarboxylation products in MeCN, such as the nature of the supporting electrolyte and its concentration, concentration of CCl_4, cathodic current density, temperature, and electric charge passed, somewhat improved the characteristics of the process.

For example, it turned out that the replacement of Et_4NBr (~0.1 *M*) rather poorly soluble in MeCN by 0.1 *M* and then 0.2 *M* Bu_4NBr solution increases the total yield of (poly)chloroacetates (*cf.* entries *1*, *2*, and *3*, Table 4) without substantial influence on their ratio. In addition, the use (entry *3*) of a 0.2 *M* solution of Bu_4NBr made it possible to decrease the cell voltage from 35 to 10 V and to reduce cathode passivation (see above) during electrolysis. Therefore, 0.2 *M* Bu_4NBr were used in further experiments.

The total yield of chloroacetates increased noticeably and the current density *j* increased from 9.4 to 18.8 mA cm^{-2} (entries *4* and *5*) with an increase in the initial concentra-

Table 4. Influence of the parameters of undivided galvanostatic electrolysis with the soluble Zn anode and steel cathode in MeCN on the yield and composition of CCl_4 electrocarboxylation (EC) products

Entry	C_{CCl_4}	Background salt C/mol L^{-1}	j /mA cm^{-2}	T /°C	Q/Q_{theor} (%)	Total yield of chhloromethyl acetates/g	Composition of EC products (yield (%))		
							MET	MED	MEM
1	0.5	Et_4NBr (0.1)	9.4	20	71.5*	1.26	77.3 (11.3)	17.0 (2.9)	5.7 (1.5)
2	0.5	Bu_4NBr (0.1)	9.4	20	71.5*	1.57	77.8 (13.7)	14.8 (3.2)	7.4 (2.2)
3	0.5	Bu_4NBr (0.2)	9.4	20	71.5*	1.60	84.0 (15.1)	9.3 (2.1)	6.7 (2.0)
4	1.5	Bu_4NBr (0.2)	9.4	20	23.8**	2.22	84.5 (7.1)	10.1 (1.0)	5.4 (0.7)
5	1.5	Bu_4NBr (0.2)	18.8	20	23.8**	3.43	84.6 (10.9)	14.9 (2.4	1.5 (traces)
6	1.5	Bu_4NBr (0.2)	18.8	10	23.8**	2.66	83.1 (8.3)	14.3 (1.8)	2.6 (traces)
7	1.5	Bu_4NBr (0.2)	18.8	-10	23.8**	1.60	88.0 (5.3)	9.1 (0.7)	2.9 (traces)

* Q_t = 9650 C (based on the two-electron process).

** Q_t = 28950 C (based on the two-electron process).

tion of CCl_4 from 0.5 to 1.5 *M* (entries *3* and *4*). For instance, in entry *5* the yield of chloroacetates was already 3.43 g instead of 1.26 g in entry *1*. At the same time, an increase in the CCl_4 concentration to the values $C_{CCl_4} \geq 3$ mol L^{-1} was accompanied by cathode passivation and an increase in the cell voltage, which induced the decrease in the yield of (poly)chloroacetates. At the current density above 18.8 mA cm^{-2} the cell voltage also increased sharply.

It is known[6] that the decrease in temperature enhances the solubility of CO_2 in an electrolyte solution, thus increasing the efficiency of electrocarboxylation. In our case, however, the temperature decrease, contrary to expectations, resulted in a consecutive decrease in the total yield of (poly)chloroacetates (*cf.* entries *5*, *6*, and *7*). Obviously, in this case, the determining factor is the decrease in the rate of chemical reactions participating in the electrode process.

Generalizing the results presented in Table 4, we can conclude that the variation of the conditions of CCl_4 electrocarboxylation in MeCN using the sacrificial zinc cathode makes it possible to obtain MET with high selectivity but exerts an insignificant effect on the ratio of the reaction products. For example, under the optimal conditions (see Table 4, entry *5*), trichloroacetate can be isolated as MET in a yield to 11% (3.2 g). Simultaneously MET is formed in the same reaction mixture in 2.4% yield (0.09 g), and only trace amounts of MEM are observed.

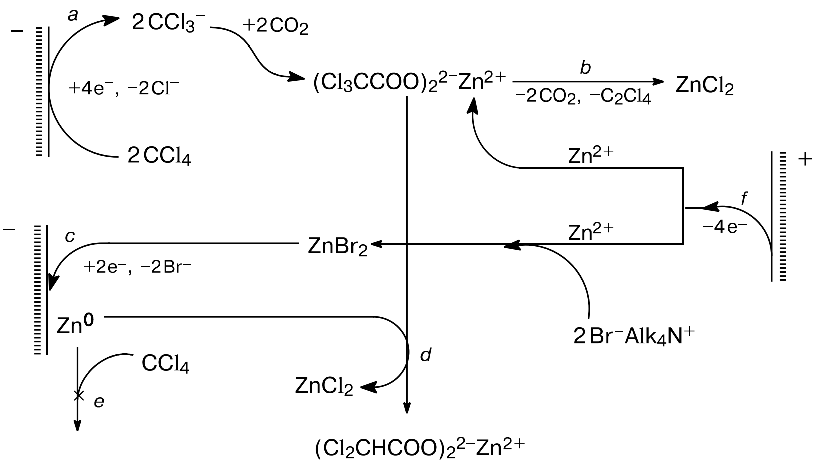
As a whole, our studies confirmed validity of the conclusions[1] that the first steps of CCl_4 electrocarboxylation resulting in the formation of zinc tri- and dichloroacetates using the sacrificial Zn anode represent rather complicated (Scheme 2) process including competitive chemical and electrochemical steps.

According to Scheme 2, step *a* corresponds to the generation of the CCl_3^- anion, whose interaction with CO_2 affords zinc trichloroacetate unstable in DMF (see Scheme 1). The fast decomposition *via* step *b* competes with the chemical reduction of trichloroacetate to the corresponding dichloroacetate (step *d*) by Zn^0 precipitated on the cathode in step *c*. These are just the reasons why no zinc trichloroacetate was observed in the electrolysis products upon CCl_4 electrocarboxylation in DMF. The major product is the corresponding dichloroacetate, which is formed in low yield along with trace amounts of zinc monochloroacetate (see Table 3, entry *1* and Ref. 1).

The reduction of anode-generated Zn^{+2} to Zn^0 (step *b*) occurs simultaneously with the reduction of CCl_4 at the cathode. The contribution of Zn^{+2} reduction depends on the solubility of $ZnBr_2$. Therefore, for electrolysis in DMF, step *b* is considerably more efficient than in MeCN (see above). It is important that Zn^0 promotes the transformation of zinc trichloromethyl acetate but cannot reduce CCl_4. Moreover, the electroreduction of CCl_4 does not occur[1] on the cathode surface covered with freshly precipitated zinc or occurs with high overvoltage.

Zinc trichloroacetate is stable in MeCN, unlike DMF. However, in MeCN the cathode is completely passivated at certain electrolysis moment. This effect imposes quantitative restrictions on the formation of zinc trichloroacetate and also prevents its further electroreduction to dichloroacetate. For these reasons, zinc trichloroacetate becomes the major product of electrocarboxylation. The variation of conditions gave more than 3 g of MET during one electrolysis with a current efficiency of 46% (based on the two-electron process), although the yield based on the initial CCl_4 was only 11% (see Table 4, entry *5*). It should be mentioned for comparison that for CCl_4 electrocarboxylation in DMF the amount of MED, which is the major product, did not exceed[1] 0.5—0.7 g even under optimal conditions.

Scheme 2



Note that because of the low solubility of $ZnBr_2$ in MeCN the contribution of steps *c* and *d* presented in Scheme 2 is insignificant and only addition of more soluble $ZnCl_2$ assist a deeper chemical reduction of zinc trichloroacetate (*cf.* entries *3* and *4,* Table 3).

Thus, the regularities of CCl_4 electrocarboxylation presented is Scheme 2 allow one to describe the mechanism of this process at the qualitative level. It is quite possible that the real process of CCl_4 electrocarboxylation is more complicated. However, we succeeded to reveal its key steps. The obtained conclusions are valid regardless of whether the primary electrocarboxylation product is $(Cl_3CCOO)_2Zn$ or $Cl_3CCOOZnCl$.

Experimental

Electrolysis was carried out in an undivided cell equipped with a thermometer, a magnetic stirrer, a cooling jacket, and a device for CO_2 bubbling including the system of its drying over H_2SO_4 followed by purification from acid traces. In addition, CO_2 flow was passed through a vessel with CCl_4 before its inlet into the electrochemical cell. As it was shown by special test, this made it possible to avoid CCl_4 losses due to blowing out when CO_2 bubbling during electrolysis.

Electrocarboxylation was carried out in the galvanostatic regime, using the B5-49 dc source and passing a specified quantity of electricity. The process was monitored with a coulometer designed at the workshop of the Institute of Organic Chemistry. A stainless steel plate (S = 42 cm^2) served as the cathode, and the anode was a Zn rod (S = 33 cm^2). Prior to electrolysis the Zn electrode was activated, namely, it was stored for 1 min in a dilute (1 : 4) aqueous hydrochloric acid, washed with distilled water, and dried.

The supporting electrolyte was a 0.1 or 0.2 *M* solution of Et_4NBr or Bu_4NBr in MeCN or DMF. Before use, quaternary ammonium salts (pure) were recrystallized from ethanol and dried by heating on a water bath of a rotary evaporator at reduced pressure for 6 h; MeCN, DMF, and tetrachloromethane were purified as described in Refs 7—9, respectively.

To identify and determine the yield of zinc (poly)chloroacetates, they were transformed into the corresponding methyl (poly)chloroacetates according to the earlier[1] developed procedure. Mixtures of the esters were analyzed by ^{1}H NMR spectroscopy (solvent DMSO-d$_6$) on a Bruker AC-200 instrument, comparing their spectra with the spectra of the authentic samples.

Synthesis of zinc trichloroacetate. Trichloroacetic acid (35.94 g, 0.22 mol) was added to a ZnO suspension (8.14 g, 0.1 mol) in water (50 mL), and the mixture was stirred until ZnO dissolved almost completely. The reaction mixture was filtered, and the mother liquor was concentrated by evaporation *in vacuo*. Residues of water and trichloroacetic acid were removed from the salt obtained by drying (8 h, 2 Torr, 50 °C). The salt was obtained in a yield of 38.26 g (98% based on ZnO). Found (%): C, 12,21; Cl, 54,67; Zn, 16,67 (average of two determinations). $C_2Cl_6O_4Zn$. Calculated (%): C, 12,29; Cl, 54,56; Zn, 16,76. ^{13}C NMR (DMSO-d$_6$), δ: 95.0 (CCl_3), 164.4 (CO).

The salt obtained was acidified with concentrated HCl followed by extraction with ether and evaporation, and trichloroacetic acid was isolated in almost quantitative yield, m.p. being 57—58 °C. The structure was confirmed by the ^{13}C NMR spectrum (DMSO-d$_6$, δ: 92.0 (CCl_3), 164.2 (CO)).

Synthesis of zinc dichloroacetate was carried out according to a similar (see above) procedure using ZnO (8.14 g, 0.1 mol) and dichloroacetic acid (28.37 g, 0.22 mol). After evaporation the mother liquor was a thick viscous syrup from which the crystalline salt (31.18 g, 97% based on ZnO) was obtained after drying (8 h, 2 Torr, 50 °C). Found (%): C, 14.99; Cl, 44.41; Zn, 20.25; H, 0.66 (average of two determinations). $C_4H_2Cl_4O_4Zn$. Calculated (%): C, 14.935; Cl, 44.183; Zn, 20.346; H, 0.622. ^{13}C NMR (DMSO-d$_6$), δ: 67.53 ($CHCl_2$), 168.31 (CO).

The following data finally convince that the zinc dichloroacetate was obtained (the elemental analysis results give some error on Zn determination): after the salt obtained it was acidified with concentrated HCl followed by extraction with ether and evaporation, dichloroacetic acid was isolated, whose structure was confirmed by the ^{13}C NMR spectrum (DMSO-d$_6$, δ: 66.3 ($CHCl_2$), 167.3 (CO)).

Testing of the stability of zinc tri- and dichloroacetates in DMF and MeCN. A weighed sample (0.005 mol) of Zn trichloroacetate (1.95 g) or Zn dichloroacetate (1.61 g) was placed in the corresponding solvent (40 mL), the mixture was stirred at room temperature for certain time (1 or 4 h), and then the solvent was distilled off at reduced pressure, and the resulting residue was weighed. The results obtained are given in Table 1.

Electrocarboxylation of CCl_4 in DMF. Experiments on electrocarboxylation in DMF are given in Tables 2 and 3 for comparison. These procedures, as well as procedures for product isolation, have earlier been described[1] in detail and remained almost unchanged when MeCN was used as the solvent.

Electrocarboxylation of CCl_4 in MeCN (general procedure using entry *5* (Table 4) as an example). A 0.2 *M* solution (100 mL) of Bu_4NBr in MeCN and CCl_4 (23.0 g, 0.15 mol) were placed in the cell, and this solution was saturated with CO_2 for 10 min. Then, continuing CO_2 bubbling, electrolysis with the current I = 0.6 A was carried out at T = 20 °C. In some experiments, additives were introduced to the electrolyte, for example, $ZnCl_2$ (2.0 g, 0.015 mol) (entry *4*, Table 3). After 6900 C charge (23.8% *Q*) was passed, the electrolysis was stopped, the electrodes were dried and weighed, and MeCN was distilled off from the electrolyte in a water bath at reduced pressure. After MeCN was removed, a solid residue containing chloroacetates, which were transformed into methyl esters of the corresponding chloroacetic acids for identification, was formed.

Methyl esters of (poly)chloroacetic acids (exemplified by entry *5*, Table 4). After MeCN was distilled off, the solid residue was dissolved in MeOH (25 mL) and treated with a solution of H_2SO_4 in MeOH (8 mL of concentrated H_2SO_4 in 50 mL of MeOH) with stirring. The mixture was stored at room temperature for 24 h, diluted with water to 500 mL, and extracted with ether (3×80 mL). The ethereal extract was washed with a saturated aqueous solution of $NaHCO_3$ and water (2×50 mL), dried for 24 h over $MgSO_4$, and filtered. The ether was distilled off, and the residue was distilled *in vacuo* (45—65 °C at 40 Torr). The product, a mixture of methyl esters of trichloro-, dichloro-, and monochloroacetic acids, was obtained (3.43 g). The methyl esters were identified by ^{1}H NMR spectroscopy (solvent DMSO-d$_6$) by comparing their spectra with the spectra of the authentic samples. Methyl trichloroacetate (MET). ^{1}H NMR (DMSO-d$_6$), δ: 4.0 (s, 3 H, OMe). Methyl dichloroacetate (MED). ^{1}H NMR (DMSO-d_6), δ: 5.9 (s, 1 H, $CHCl_2$); 3.85 (s, 3 H, OMe). Methyl chloroacetate (MEM). ^{1}H NMR (DMSO-d_6), δ: 4.22 (s, 2 H, CH_2Cl); 3.72 (s, 3 H, OMe).

The composition of the isolated MET—MED—MEM (84.6 : 14.9 : 1.5%) mixture of products was determined on the basis of the ratio of integral intensities of signals from the methoxy groups. The substance yield of MET was 11% and the current efficiency was 46% (based on the two-electron process).

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