Electrolysis of *a*-Chloro- and *a*-Fluorocarboxylic Acids

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The electrolysis of α -chlorovaleric, α -chlorocaproic, and α -chloroisobutyric acids in methanol gave none of the Kolbe dimer; the main products were chloroester and hydrogen ester with aldehydes and acetals formed in lesser amounts. In water, straight chain α -chloroacids gave dimeric esters as the major product. However, Kolbe dimer was formed in fairly good yields together with small amounts of fluoroester and acetal, when α -fluorocaproic and α -fluoroheptanoic acids were electrolyzed in methanol. No Kolbe dimer was produced from 2-fluoro-2-ethylbutanoic and α -fluorophenylacetic acids; the corresponding ketone or aldehyde was the major product.

Les électrolyses dans le méthanol des acides α -chlorovalérique, α -chlorocaproïque, et α -chloroisobutyrique ne conduisent pas aux dimères de Kolbe; les produits principaux sont les chloro-esters et les hydrogénoesters; en plus petite quantité se forment des aldéhydes et des acétals. Dans l'eau, les α -chloroacides en chaine droite conduisent aux esters dimériques en tant que produits majoritaires. Cependant, dans l'électrolyse dans le méthanol des acides α -fluorocaproïque et α -fluoroheptanoïque, des dimères de Kolbe se forment avec un assez bon rendement avec toutefois de petites quantités de fluoro-esters et d'acétals.

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In a previous paper (1) from this laboratory, the electrolysis of α -bromocarboxylic acids in methanol produced hydrogen ester and bromoester as major products. The results were regarded as the result of attack of an initial carboxy radical on the solvent. Reduction of C-Br to C-H in both the ester and acid occurred at the cathode with migration of Br⁻ to the anode and oxidation there to Br₂. Electrolysis experiments with branched chain α bromoacids in water indicated production of carbonium ions. In all the acids studied, no Kolbe dimer was detected, nor were other possible products such as alcohols, ethers, and paraffins obtained. Hoping to understand better the electrochemical processes involved with α -halo substituents, the behavior of α -chloroand α -fluorocarboxylic acids during Kolbe electrolysis was examined. It was anticipated especially that the smaller, more stable fluorosubstituent might allow dimer formation to occur. Conway and Dzieciuch (2) previously found that normal Kolbe coupling took place

with trifluoroacetic acid; this reaction was the only previous example of successful coupling with an α -fluoro substituent present.

The electrolyses of α -chlorocarboxylic acids were carried out in methanol and water. The results of various electrolysis reactions of α chlorovaleric, a-chlorocaproic, and a-chloroisobutyric acids in methanol (Scheme 1) are summarized in Table 1 and show that chloroester is the major organic product. Hydrogen ester is formed in low yields with the ratio of hydrogen ester to chloro ester increasing as the time of electrolysis is increased. The straight-chain α-chloroacids also produced acetals in low yield but this behavior was not observed with the branched-chain acid. It is probable that the corresponding acetal was formed from the branched-chain chloroacid, but because of volatility was lost under the experimental conditions used.

The presence of 1-chloropentane in trace amounts in the electrolysis products of α -chlorocaproic acid shows that, at least in part, radical

$$\begin{array}{cccc} Cl & Cl & H \\ R_1R_2 - C - COOH & \xrightarrow{CH_3OH} R_1R_2 - C - COOCH_3 + R_1R_2 - C - COOCH_3 + R_1 - CH(OCH_3)_2 + Cl_2 \\ (Chloroacid) & (Chloroester) & (Hydrogen ester) & (Acetal, R_2 = H) \end{array}$$

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Acid used (10 g)	Solvent (ml)	Current (A)	Time (h)	Temperature (°C)	Weight of neutral fraction (g)	Weight of acidic fraction (g)	Yield % of			
							Chloro ester	Hydrogen ester	Acetal	
α-Chlorovaleric acid	30	0.8	6	45	2.8	6.7	60	trace	2.4	
	30	1.0	18	45	2.9	6.5	63	trace	trace	
	50	0.6	24	30	2.9	6.0	24	6.2	5.0	
	50	1.1	24	34	4.5	5.1	45	11	9.9	
α-Chlorocaproic acid	30	0.6	8	35	2.3	6.5	41	nil		
	30	1.0	12	6	2.0	6.9	41	5.1	6.9*	
	30	1.2	$\overline{24}$	38	4.2	1.8	24	7.3	7.2*	
	35	0.7	24	37	6.3	2.3	23	19	14	
α-Chloroisobutyric acid	30	0.8	6	35	0.7	8.6	30	5.5		
	30	0.8	12	32	1.1	8.8	37	4.4		
	60	1.0	-6	30	1.2	8.3	24	8.1		
	30	Ô.8	24	35	4.4	5.3	65	11		

TABLE 1. Electrolysis of α -chlorocarboxylic acids in methanol

*Approximately 2% free aldehyde also isolated in these cases. Trace amounts of 1-chloropentane were also found.



was converted to saturated chloroalkane. Such behavior was not observed in the case of α -chlorovaleric or α -chloroisobutyric acid. Divided cell and control experiments for the chloroacids similar to those conducted for the bromoacids showed essentially the same results. Reduction of C—Cl to C—H occurred at the cathode, with Cl⁻ migration to the anode and formation there of Cl₂. Esterification occurred at the anode only, whereas some of the side products such as aldehydes and acetals were found in the cathode compartment. Control experiments on esterification (with no electrolysis) showed that prolonged heating of α -chloroacids in methanol produced very little (*ca.* 5–8%) ester.

In water, α -chlorovaleric and α -chlorocaproic acid (straight-chain acids) behaved differently from the analogous α -bromoacids. With the straight-chain chloroacids the major electrolysis product was 1'-chloro-1'-butyl 2-chloropentanoate (40%) from α -chlorovaleric acid and 1'chloro-1'-pentyl 2-chlorohexanoate (38%) from a-chlorocaproic acid. Such esters were not isolated from *a*-bromoacids. No Kolbe dimer was detected, nor were other possible esters found (*i.e.* those in which one or two $C--Cl \rightarrow C--H$ conversions occurred); some unidentified high molecular weight compounds were also produced. The formation of esters in electrolysis reactions in water can be explained by combination of carboxy and alkyl radicals absorbed on the electrode surface and is consistent with mechanisms proposed by Troeger and Ewars (3) and Kaufler and Herzog (4). Alternatively a further oxidation of the alkyl radical could occur yielding the corresponding carbonium ion, which would

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give the same ester by combination with the initial carboxylate anion (Scheme 2). Carbonium ions are usually produced only when secondary or tertiary species can form (a good general discussion of radical and carbonium ion intermediates during Kolbe electrolysis may be found in recent work by Skell and coworkers (ref. 5 and articles cited therein) and by Eberson (6)). Perhaps in this case some stabilization by the resonance form $CH_3(CH_2)_n$ —CH== Cl^+ may be involved. Such ester formation from a carbonium ion intermediate avoids the involvement of a carboxy radical which is known to have a short lifetime (ca. 10^{-9} s) in chemical processes, although it is believed to be longer-lived when absorbed on a platinum electrode. Lack of Kolbe dimer from these α -chloroacids would also be consistent with a carbonium ion species. The present results also indicate that the C--Cl bond is more stable than C-Br in the α-bromoacids and there is negligible or very little reduction of this C-Cl bond during electrolysis.

Electrolysis in water of α -chloroisobutyric acid (a branched-chain acid) produced mainly ketones rather than esters. Products obtained were acetone (18.3%), 1,1-dichloroacetone (2.4%), and 1,3-dichloroacetone (0.8%). As discussed for the bromo analog, it is likely that acetone was the major reaction product at the electrode but, being miscible in water and very volatile, either reacted further with chlorine or was lost in the exit gas stream. Some high molecular weight substances were also formed which could not be obtained pure. The similarity of products from electrolysis of a-chloroisobutyric acid in water and the corresponding *a*-bromoacid reported earlier (1) indicates that product formation can be interpreted in terms of the production of a carbonium ion $(CH_3)_2 \overset{+}{C}$ —Cl which picks up OH⁻ from water with the ketone resulting.

$$CH_{3}(CH_{2})_{n} - CH - COO^{-} \xrightarrow{-e} CH_{3}(CH_{2})_{n} - CH - COO \cdot \xrightarrow{-CO_{2}} CH_{3}(CH_{2})_{n} - CH \cdot \xrightarrow{-e} CH_{3}(CH_{2})_{n} - CH^{+}$$

SCHEME 2

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TABLE 2.	Electrolysis of α -fluorocaproic acid in methanol					
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Acid used (10 g)				Fime Temperature (h) (°C)	Weight of neutral fraction (g)	Weight of acidic fraction (g)	Yield % of				
	Solvent (ml)	Current Ti (A) (Time (h)				Fluoro ester 2	Hydrogen ester 3	Acetal 4	Kolbe dimer 5a	Kolbe dimer 5b
α-Fluorocaproic acid	30 30 30 30 30 30	0.8 0.8 0.8 0.8 1.0	6 12 24 12 12	35 32 30 43 6	3.8 5.4 4.8 5.0 4.3	1.5 1.8 2.3 1.0 2.5	4.2 6.4 12 4.4 7.7	1.6 nil trace nil 	7.0 27 20 4.4 19	16 19 12 32 20	17 20 17 33 20

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 α -Bromo- and α -chloro-substituted acids did not produce normal Kolbe coupling reactions and while similar to some extent in their reactions, the chloro-substituent was not as easily lost by reduction to C—H. Therefore it seemed reasonable to ascertain if a halogen atom smaller in size would allow dimer formation (also a C—F bond would be expected to be even less easily converted to C—H). As a start, efforts were concentrated on α -fluorocaproic acid. The results of various electrolysis reactions of this fluoroacid in methanol are given in Table 2 and products are illustrated in Scheme 3.

Fluoroester 2 was produced in poor yield compared to the analogous chloroester and the acetal yield was variable. The major products were diffuorides 5a and b. Both showed essentially identical n.m.r. absorption attributable to methyl at 9.03 τ , methylene at 8.4 and 8.2 τ and methine, four broad multiplets centered at 5.7 τ (gem $J_{\rm HF} \sim 50$ and vic $J_{\rm HF} \sim 20$ Hz); both showed similar i.r. absorption at 1060 (C—F) cm^{-1} . This evidence in conjunction with microanalytical data confirms structure 5 and indicates the two dimers are the anticipated diastereomers formed in essentially equal amounts. Both these compounds appeared as two separate peaks (g.l.c.) and could easily be isolated at temperature programming of 170–190°. Further efforts to distinguish between these diastereomers were not attempted. Monomeric 1-fluoropentane CH₃(CH₂)₃CH₂F was anticipated as a possible product but no trace was found. In all the electrolyses of α -fluorocaproic acid, changes in concentration and time appeared to have little effect but at higher temperature the ratio of dimeric compounds to other products is increased. 1,1-Dimethoxypentane, 4, formed in ca. 20% yield was identified by its n.m.r. and i.r. spectra and comparison of its g.l.c. retention

time with an authentic sample. A small quantity of valeraldehyde was also detected by g.l.c.

To determine how typical dimer formation was during Kolbe electrolysis, we decided to extend our study to some other α -fluoroacids, *viz.* α -fluoroheptanoic acid, 2-fluoro-2-ethylbutanoic acid, and α -fluorophenylacetic acid. Electrolysis of α -fluoroheptanoic acid in methanol gave the Kolbe dimer 6,7-difluorododecane (both diastereomers),

Structures were confirmed as in the previous case. On the other hand the branched-chain fluoroacid, 2-fluoro-2-ethylbutanoic acid, gave 3-pentanone (24-32%) as major electrolysis product as well as the expected fluoroester (6-9%). Several electrolyses of this acid in methanol revealed that changes in temperature, current density, temperature, concentration, or time did not result in dimer formation. Similar behavior was observed when α -fluorophenylacetic acid was electrolyzed where the only product formed was benzaldehyde (for comparison, the corresponding a-bromophenylacetic acid gave hydrogen ester as major product (80%) along with very little (2.5%) bromoester but essentially no benzaldehyde). The lack of dimer formation from these latter two acids is not surprising since carbonium ion formation leading to carbonyl products is much more likely.

The work described herein represents the first detailed study of the electrolysis of α -chloro and α -fluorocarboxylic acids. The results for α -chloro-acids in methanol are essentially the same as for α -bromoacids, except that the reduction of C—Cl is less pronounced in the chloroacids. In water the straight-chain α -chloroacids produced

esters. With the α -fluoroacids the straight-chain α -fluoro-caproic and -heptanoic acids produced the Kolbe dimers possibly because the fluorine atom being smaller allows the

linkage to form more easily. Also C—F is less easily reduced to C—H. The difluoro dimer should also be more stable under electrolysis conditions, since Br_2 and Cl_2 can be lost¹ from the appropriate dihalide but not F_2 from the difluoride.

Experimental

General

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 α -Chlorovaleric acid (7, 8), α -chlorocaproic acid (7, 8), and α -chloroisobutyric acid (9) were prepared according to methods described in the literature. The fluoroacids were synthesized according to the method of Pattison et al. (10, 11) but yields on large scale preparations were poor especially for the branched-chain acid. Microanalyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, New York. The g.l.c. analyses and separations were carried out on an Aerograph Autoprep model 700 with a $10' \times 3/8''$ column with a 30% loading on Chromosorb W of either silicon gum rubber SE-30 or Carbowax 20M. Temperature programming was used in the range 170-250°. Detector temperature was kept ca. 25° above the column temperature when collection of the sample was desired. The i.r. spectra were taken with a Beckman IR-10 spectrophotometer either on thin liquid films or in CCl₄ solution. The n.m.r. spectra were obtained with a Varian T-60 spectrometer, absorptions being quoted in τ values against tetramethylsilane.

The conventional electrolysis cell, general method of electrolysis, isolation of products, and divided cell experimental details have been described before (1, 12).

Electrolysis of α -Chloro Acids in Methanol

The results of these electrolyses at various temperatures and concentrations are found in Table 1. The products were identified by comparison with authentic samples, especially in their g.l.c. behavior and i.r. spectra.

For comparison, certain control reactions were run. Refluxing of α -chloro acids under electrolysis conditions, but with no current resulted in some esterification (10–13%). Prolonged heating (40–50°) of α -chloro acids (no electrolysis) gave no conversion to hydrogen acid but did produce some (5–8%) esterification. However, when some methyl α -chloroesters were subjected to electrolysis (under similar condition to those shown in Table 1), they gave considerable amounts of the appropriate hydrogen esters (35–40%). Electrolysis of α-Chlorovaleric and α-Chlorocaproic Acids in Water

Potassium hydroxide (4.2 g, 0.075 mol) was dissolved in water (60 ml) and α -chlorovaleric acid (25.5 g, 0.187 mol) was added. A current of 1.25 A was passed for 40 h and the temperature was kept at 10–15° with an ice bath. After isolation of neutral and acidic fractions in the usual manner, a light brown neutral oil (12.9 g) was collected. The neutral fraction showed (g.l.c.) a major fraction (40%); a small sample of this compound was isolated with the Autoprep-700 using an SE-30 column, temperature programming from 160–200°, and a detector temperature of 250°, and was identified as 1'-chloro-1'-butyl 2-chloropentanoate. The i.r. spectrum showed strong absorption at 1770 cm⁻¹ (CCl₄). The n.m.r. spectrum showed peaks at τ 9.1, 8.8, 5.9, and 3.8 with integrated areas of 6:4:4:1:1. The triplet at τ 5.9 indicated

whereas the triplet at τ 3.8 indicated

Anal. Calcd. for $C_9H_{16}O_2Cl_2$: C, 47.60; H, 7.51; Cl, 31.24. Found: C, 47.85; H, 7.15; Cl, 31.18.

Similarly α -chlorocaproic acid (31.0 g, 0.2 mol) was electrolyzed at 1.2 A for 36 h. A dark brown neutral oil (14.1 g) was collected which when subjected to fractional distillation under reduced pressure decomposed. From a fresh sample of neutral oil 1'-chloro-1'-pentyl 2-chlorohexanoate was isolated by g.l.c. This ester has the same spectral features as 1'-chloro-l'-butyl 2-chloropentanoate.

Anal. Calcd. for $C_{11}H_{20}O_2Cl_2$: C, 51.78; H, 7.84; Cl, 27.81; Found: C, 51.87; H, 7.74; Cl, 28.00.

Electrolysis of a-Chloroisobutyric Acid in Water

 α -Chloroisobutyric acid (30.6 g, 0.25 mol) was added to a solution of potassium hydroxide (5.7 g) in water (65 ml). A current of 1.5 A was passed for 28 h and the temperature was kept at 20–25°. Work-up as usual gave 9.4 g of neutral product, which was mainly acetone (18.3%), 1-chloroacetone (6.1%), 1,1-dichloroacetone (2.4%), and 1,3-dichloroacetone (0.8%).

Electrolysis of α -Fluorocaproic and α -Fluoroheptanoic Acids in Methanol

The results of several electrolyses of α -fluorocaproic acid are shown in Table 2. The fluoroester was confirmed by use of an authentic sample. Hydrogen ester was absent. Three other components were isolated by g.l.c. using the SE-30 column, temperature programming of 170–190°, and a detector temperature of 220°. One component was identified as 1,1-dimethoxypentane CH₃(CH₂)₃—CH(OCH₃)₂. The i.r. spectrum in CCl₄ solution showed bands at 1050 and 1130 cm⁻¹; the n.m.r. spectrum showed four groups of peaks at τ 8.9, 8.7, 6.8, and 5.8 with relative intensities of 3:6:6:1. This compound had identical g.l.c. behavior when compared with an authentic sample prepared according to the method of Lorette and Howard (13). The other two components appeared from the elemental analysis to be diasterioisomers.

¹We have observed the loss of Br_2 under our electrolysis conditions from *vic*-dibromoacids but have not done any detailed studies. Other than studies on α,β -dihaloacids, there are not many recorded examples in this area.

Anal, Calcd, for

C, 67.41; H, 11.23; F, 21.34. Found for one diastereomer: C, 67.18; H, 11.00; F, 21.72. Found for the other diastereomer: C, 67.77; H, 11.61; F, 21.32.

The i.r. spectrum in each case showed a band at 1060 (C—F) cm⁻¹. The n.m.r. spectra of each isomer showed signals for methyl at 9.03 τ , methylene at 8.4 and 8.2 τ , and methine, four broad multiplets centered at 5.7 τ (gem $J_{\rm HF}$ 50 and vic $J_{\rm HF}$ 20 Hz). The refractive indices of these diastereomers were very similar ($n_{\rm D}^{24}$ 1.4018 and 1.4027 respectively); the first isomer remained a colorless oil on cooling in ice but the second isomer solidified.

Similar electrolysis of α -fluoroheptanoic acid was carried out in methanol under identical conditions with that of α -fluorocaproic acid. The neutral fractions from three runs were examined only for dimeric compounds which constituted *ca.* 40–60% of the neutral fraction. Two compounds were isolated with the Autoprep Model 700, in a similar fashion to the isolation of the two diasterioisomers obtained from the electrolysis of α -fluorocaproic acid (g.l.c., two separate peaks).

Anal. Calcd. for

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$$\begin{array}{c} F & F \\ | & | \\ CH_3(CH_2)_4 - CH - CH - (CH_2)_4 - CH_3, (C_{12}H_{24}F_2): \end{array}$$

C, 69.90; H, 11.65; F, 18.90. Found for one diastereomer:

C, 69.56; H, 11.65; F, 18.50. Found for the other diastereomer: C, 69.72; H, 11.82; F, 18.58.

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