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ELECTROCHEMICAL POLYMERIZATION OF DICARBOXYLIC ACIDS—V. EFFECT OF CHAIN LENGTH BETWEEN THE CARBOXYL GROUPS

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Abstract—The electrochemical polymerizations of suberic and azelaic acids were investigated in methanol: pyridine (1:1) and the results compared with those previously obtained for adipic and sebacic acids, to find out the effect of chain length between the carboxyl groups on formation of polymer and oligomeric side products. On passing from adipic to sebacic acid, the ratio of hydrocarbons formed to polymer decreased, polymer yield increased a little, and the extent of decarboxylation increased indicating a greater hydrocarbon structure to the polymers. This is reflected in the properties of the polymers; that obtained from adipic acid was degraded considerably on alkaline hydrolysis unlike those obtained from azelaic and sebacic acids which remained insoluble and high melting.

INTRODUCTION

In previous work [1–4] we studied in detail the electrochemical polymerization of adipic acid and sebacic acid; certain differences were observed. To obtain a clear picture of the effect of the chain length between the two carboxyl groups on formation of polymer and side products, we studied the electrochemical polymerizations of two homologues viz. suberic acid $(CH_2)_6(COOH)_2$ and azelaic acid $(CH_2)_7(COOH)_2$ and compared the results obtained with the other dicarboxylic acids. The electrolyses were carried out in methanol:pyridine (1:1) which was found to be optimal for the reaction.

EXPERIMENTAL

The electrolyses were carried out as reported previously [1, 2] and the same methods of separating and analyzing the products were used.

RESULTS AND DISCUSSION

Electrolysis of suberic acid (Table 1)

The molar amount of CO_2 evolved was proportional to the number of coulombs passed; after passage of 7166 coulombs, 40.16 mmol CO_2 were evolved, meaning 5.6×10^{-6} mol/coulomb. The gases evolved, excluding CO_2, were 39.86 mmol. The theoretical amount of H_2 that should be evolved for this number of coulombs is 37.13 mmol; the difference of 2.73 mmol is due to the ethylene formed from electrolysis of the triethylamine [4].

After neutralization of the pyridine in an aliquot of the reaction mixture and extraction with methylene chloride, the extract was analyzed for volatile products by GC on a 20% squalane column at 50°. Seven peaks were found, identified by GCMS and quantitatively determined. Five of them belonged to C_6 hydrocarbons; their yield was 3.03 mmol (12% based

Table 1. Balance of the products obtained in the electrolysis of suberic acid in methanol:pyridine (1:1)*

$(CH_2)_{6n}$-X n	Hydrocarbons mmol	(%)	Methyl esters mmol	(%)	Methyl ethers mmol	(%)	Carboxylic acids mmol	(%)	Suberic acid (%)
1	3.03	(12.0)	0.42	(1.7)†	0.14	(0.6)	0	(0)	14.3
2	0.86	(6.9)	0.09	(0.7)	0.23	(1.8)	0.67	(5.4)	14.8
3	0.31	(3.7)	0.04	(0.5)	0.06	(0.7)	0.35	(4.2)	9.1
4	0.13	(2.0)	0.03	(0.4)	0.04	(0.6)	0.59	(9.4)	12.4
5	0.04	(0.8)	0.01	(0.2)	0.02	(0.3)	0.17	(3.4)	4.7
6	0.01	(0.2)	0	(0)	0	(0)	0.08	(1.9)	2.1
		25.6‡		3.5‡		4.0‡		24.3‡	
					Benzene fraction, yield				3.0
					Methanol fraction, yield				6.0
					Polymer, yield				30.0
					Total yield of recovered products				96.4

*Suberic acid (5.22 g, 30 mmol) was dissolved in methnanol:pyridine (1:1 by volume) (30 ml) triethylamine (3 mmol) was added, and the electrolysis carried out at 1.2 A current and stopped when the current dropped to 0.8 A, after passing 7166 coulombs; 83.5% of the suberic acid reacted. The percentage given under every product is that of the reacted suberic acid converted into that product. The last column gives the percent of suberic acid converted to products having the same n (degree of oligomerization). The structure of the products was taken as $(CH_2)_{6n}$ for the hydrocarbons, $(CH_2)_{6n}COCH_3$ for the methyl esters, $(CH_2)_{6n}OCH_3$ for the methyl ethers, and $(CH_2)_{6n}COOH$ and/or $HOOC(CH_2)_{6n}COOH$ for the carboxylic acids.
†Composed of C_7 methyl esters (0.31 mmol) and γ- and δ-C_7 lactones (0.11 mmol).
‡Total yield of that type of product.

Table 2. Composition of the hydrocarbon fractions obtained in the electrolysis of suberic acid in methanol:pyridine (1:1)*

	% Composition by weight				
Hydrocarbons	*n*-alkane	1-alkene	*x*-alkene	cycloalkane	1,*x*-alkadiene
C_{12}	7.3	18.6	21.6	38.5	14.0
C_{18}	11.8	27.4	30.6	15.2	15.0
C_{24}	14.8	28.4	47.2	9.6†	—
C_{30}	93.7‡	—	—	6.3	—

*Electrolysis carried out on 30 mmol suberic acid as in Table 1. The hydrocarbons were determined by GC on 5% butane diol succinate.
†Includes 1,*x*-alkadiene that was not separated.
‡Includes 1-alkene and *x*-alkene that were not separated.

on the suberic acid reacted) divided as follows: 1-hexene (38%), *x*-hexene (the position of the double bond not known (6%), *n*-hexane (15%), 1,5-hexadiene (12%) and cyclohexane (29%) (Table 1). The other two peaks were identified as a saturated methyl ether $CH_3O(CH_2)_5CH_3$ and its unsaturated isomer, $CH_3O(CH_2)_4CH{=}CH_2$ formed in a 1:2 ratio respectively in 0.6% yield. After the seventh peak had passed, the column was heated at 4°C/min up to 100°C and two other peaks appeared belonging to saturated and unsaturated methyl esters of C_7 carboxylic acids in a 1:2 ratio respectively.

$C_{1,x}$-alkadienes, such as C_{12}, were identified on the basis of the fragmentation pattern; they contained one double bond at the end of the chain and the other in the middle with position unknown. The yield of the hydrocarbons decreased with increasing molecular weight (Table 1). The cycloalkane fraction was very high at C_{12} (39%) and decreased to 6.3% of the total hydrocarbons at C_{30} (Table 2).

The front benzene fraction contained methyl esters and methyl ethers, both saturated and unsaturated, the latter being the more abundant. Three types of ethers were formed viz.

$$CH_3OCH(CH_3)(CH_2)_{6n-4}CH{=}CH_2;\quad CH_3O(CH_2)_{6n-1}CH_3;$$

$CH_3O(CH_2)_4CH{=}CH(CH_2)_{6n-7}{-}CH_3$ with a *trans* configuration. The ether fraction was obtained in 4.2% yield and that of the ester in 3.4% (Table 1).

The carboxylic acid fraction was extracted from the reaction mixture by KOH as before [2] and identified by GCMS after methylation; 16.5% of unreacted suberic acid was found. Saturated and unsaturated mono acids in a 1:1 ratio as well as diacids up to C_{38} were identified. The amounts of the monoacids, given in parenthesis in mmol, were: C_{13} (0.25), C_{19} (0.11); C_{25} (0.08), C_{31} (0.07), C_{37} (0.07); those of the diacids were: C_{14} (0.42), C_{20} (0.19), C_{26} (0.48), C_{32} (0.09), C_{38} (0.05) (Table 1). The overall yield in the acid fraction was high at about 24%, which is similar to that found with sebacic acid [4]. Relatively high oligomeric mono- and di-acids were also formed, noteworthy the diacid (n = 4) which was formed in relatively high yield (7.7%).

The higher oligomeric products were separated as described [2] by column chromatography and divided into 4 fractions viz. that eluted by heptane, the front-benzene fraction, the benzene fraction and the methanol fraction.

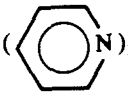
The heptane fraction (0.3 g) as seen from i.r. and NMR contained only hydrocarbons. Separation on a column of butane diol succinate showed (Table 2) that they were composed of *n*-alkanes, 1-alkenes, *x*-alkenes, 1,*x*-alkadienes and cycloalkanes. The

The benzene fraction (3% yield) contained some volatile products. Two major peaks in GC were identified from their MS as γ- and δ-C_7 lactones (0.11 mmol), the γ-lactone being 68% of the fraction. i.r. And NMR of the benzene fraction (excluding the contribution of the lactones) showed the following groups:

$$(CH{=}CH)_1\ (trans);\quad (CH{=}CH_2)_2;\quad (-CH_2OC({=}O))_3;\quad (CH_3OC({=}O))_3;\quad (CH_3OCH_2)_1;\quad (CH_2)_{10}{-}X;$$

$(CH_2)_{61}$; $(CH_3)_3$. If all the partial structures are joined, the structural formula obtained is $C_{94}H_{179}O_{13}$ and, after taking off the groups that do not originate from suberic acid, the structure reduces to $C_{90}H_{167}O_{12}$ or $[(CH_2)_6]_{14}(COO)_6$ which indicates the extent of decarboxylation was 78%. The ratio CH_2/X, showing the average number of methylene groups/functional or terminal group is 8.4.

The methanol fraction (6% yield) had no volatile product in GC. i.r. And NMR showed the following groups:

$$(CH_2{=}CH)_1;\quad (CH_2OC({=}O))_4;\quad (CH_3OC({=}O))_2;\quad (CH_2)_{10}{-}X;\quad (CH_2)_{59};\quad (CH_3)_2;\quad (COOH)_2;\quad ($$  $$)_1.$$

This leads to the general formula $C_{94}H_{172}O_{17}N$ (M = 1586) and, after subtracting the groups not originating from suberic acid, we obtain $[(CH_2)_6]_{13}(COO)_8$, i.e. 69% decarboxylation. The ratio $CH_2/X = 5.6$.

Table 3. Balance of the products obtained in the electrolysis of azelaic acid in methanol:pyridine (1:1)*

$(CH_2)_{7n}$–X	Hydrocarbons		Methyl esters		Methyl ethers		Carboxylic acids		Azelaic acid
n	mmol	(%)	mmol	(%)	mmol	(%)	mmol	(%)	(%)
1	3.51	(14.5)	0.32	(1.3)†	0.12	(0.5)	1.60	(6.6)	22.9
2	0.89	(7.4)	0.05	(0.4)	0.13	(1.0)	0.77	(6.4)	15.2
3	0.37	(4.6)	0.02	(0.25)	0.06	(0.7)	0.32	(0.4)	9.5
4	0.14	(2.3)	0.008	(0.13)	0.01	(0.2)	0.14	(2.3)	4.9
5	0.02	(0.1)	0	(0)	0	(0)	0	(0)	0.1
		28.9		2.1		2.4		19.3	
					Benzene fraction, yield				3.0
					Methanol fraction, yield				5.4
					Polymer, yield				32.0
					Total yield of recovered products‡				93.0

*Azelaic acid (5.64 g, 30 mmol) was dissolved in 30 ml methanol:pyridine (1:1), triethylamine (3 mmol) was added, and the electrolysis carried out at 1.1 A, and stopped after pasing 7641 coulombs; 81% of the azelaic acid reacted. Yields based on reacted azelaic acid. See Table 1 for explanation of the headings.
†Composed of C_8 methyl esters (0.19 mmol) and γ- and δ-C_8 lactones (0.13 mmol).
‡Does not include 8.5 mg of unidentified products, from the front-benzene fraction.

The polymer fraction (yield 0.9 g, 30%) had an i.r. spectrum similar to that of the methanol fraction. According to microanalysis, the general formula of the repeat unit is $C_{144}H_{240}O_{29}N$ (M = 2446). The polymer contained 3.8×10^{-3} mol ester groups, 0.28×10^{-3} mol COOH groups and 3.68×10^{-3} mol methoxy groups/1 g polymer, % decarboxylation = 75%. On hydrolysis in KOH/ethylene glycol, the polymer suffered partial degradation and a loss of weight of 23%.

The average decarboxylation in the electrolysis based on CO_2 evolved and suberic acid reacted was 80%. The major products in the electrolysis were polymer (30%), hydrocarbons (26%) and acids (24%).

Electrolysis of azelaic acid (Table 3)

The rate of evolution of CO_2 was proportional to the number of coulombs passed and the proportionality factor was 5.2×10^{-6} mol CO_2/coulomb. The C_7 hydrocarbons were isolated as before in the volatile fraction and analyzed. The compositon was 1,6-heptadiene (10%), 1-heptene (39%); *n*-heptane (14%), *x*-heptene (3%), cycloheptene (29%) and bicyclo (1:2:2) heptane (5%). The bicyclo type of product was not found in the electrolysis of other dicarboxylic acids. Here it was identified from its mass spectrum: molecular peak at m/e = 96; basic peak at m/e = 67 and strong peak at m/e = 68. The volatile fraction contained also two ethers, $CH_3O(CH_2)_6$–CH_3 and $CH_3O(CH_2)_5CH{=}CH_2$ (0.12 mmol), in a 1:2 ratio respectively. On further heating of the column, two peaks appeared identified as belonging to two C_8 methyl esters, saturated and unsaturated in a ratio of 2:1 (together 0.19 mmol).

The acid fraction contained saturated and unsaturated mono acids approximately in a 1:1 ratio as follows (amounts given in mmol): C_8 (1.6); C_{15} (0.64), C_{22} (0.24), C_{29} (0.09). The diacids formed C_{16} (0.13); C_{23} (0.08); C_{30} (0.05). The total acids were obtained in 19% yield, the C_8 mono acids in 6.6% and the C_{15} in 5.3%.

The higher oligomeric products were separated by column chromatography as before. The heptane fraction was analyzed by GCMS. Two groups of 4 peaks were found belonging to C_{14} and C_{21} hydrocarbons. Every group consisted of *n*-alkane, 1-alkene, *x*-alkene and cycloalkane. The composition of the C_{14} hydrocarbons was 17% *n*-alkane, 33% 1-alkene, 27% *x*-alkene and 23% cycloalkane and that of the C_{21} hydrocarbons was 19% *n*-alkane, 45% 1-alkene, 22% *x*-alkene and 13% cycloalkane. The C_{28} hydrocarbons were composed of 87% straight chain products and 13% cycloalkane.

The front benzene fraction contained a mixture of saturated and unsaturated methyl esters in approximately 1:1 ratio as well as saturated and unsaturated methyl ethers. The yield of the esters was 2% and of the ethers 2.5% (Table 3).

The benzene fraction had a GC volatile fraction which showed two strong peaks, identified from their MS as γ- and δ- C_8 lactones (0.13 mmol); the γ was the major fraction (65%). i.r. And NMR of the residual benzene fraction gave the general formula $C_{101}H_{194}O_{13}$ and, after subtracting the groups not originating from azelaic acid, the formula reduces to $C_{91}H_{182}(COO)_6$ or $[(CH_2)_7]_{13}(COO)_6$, i.e. 77% decarboxylation. The ratio of functional groups to $-CH_2-$ groups (CH_2/X) was 9.1 and the yield of the benzene fraction was 3%.

The methanol fraction did not contain any volatile products. i.r. And NMR showed that the general formula is $C_{125}H_{233}O_{21}N$ (M = 2083) and, after subtracting the groups not originating in azelaic acid, the formula reduces to $[(CH_2)_7]_{15}(COO)_9$, i.e. 70% decarboxylation. The ratio CH_2/X is 7.5 and the yield 5.4%.

The polymer fraction (yield 1.1 g, 32%) had the same type of groups as the methanol fraction (i.r.). Elemental analysis led to the structural formula of the recurring unit as $C_{145}H_{258}O_{25}N$ (M = 2412). The polymer contained 2.66 mmol esters groups, 0.19 mmol COOH groups and 4.56 mmol methoxy/g polymer. The percent decarboxylation was 79%. The polymer on hydrolysis in KOH/ethylene glycol lost 14% in weight, but kept its properties, melting point (>300°) and insolubility.

The overall decarboxylation in the electrolysis was 82%, based on the CO_2 evolved and the amount of azelaic acid reacted. The main products of the reaction were polymer (32%), hydrocarbons (29%) and carboxylic acids (19%) (Table 3).

Table 4. Electrolysis of dicarboxylic acids in methanol:pyridine (1:1)*

Acid	Current passed, (C)	Acid reacted, (%)	$K'(CO_2)$† (C/mol $\times 10^{-6}$)	Overall Decarb. (%)	C_KHC, (%)	% Acid reacted ($C \times 10^{-3}$)	HC/ Polymer	Polymer Yield, (%)	Polymer Decarb. (%)	Benzene fraction Yield (%)	Benzene fraction Decarb. (%)	$(CH_2)/X$	Methanol fraction Yield, (%)	Methanol fraction Decarb. (%)	$(CH_2)/X$
Adipic, $K = 4$	8536	89.4	5.1	81	24	10.4	1.23	31	70	4.0	83	8.0	6.0	74	4.8
Suberic $K = 5$	7166	83.5	5.6	80	12	11.7	0.88	29	75	2.6	78	8.4	6.0	69	5.6
Azelaic $K = 7$	7641	81.0	5.2	82	14.5	10.6	0.86	32	79	3.0	77	9.1	5.4	70	6.2
Sebacic $K = 8$	6485	68.0	4.8	76	15	10.5	0.69	35	79	3.0	73	9.5	8.5	66	8.0

*Acid (30 mmol) was dissolved in 30 ml methanol:pyridine (1:1), triethylamine (3 mmol) added and the electrolysis carried out at 1.3 A, current density 0.2 A/cm^2; the direction of the current was reversed every 90 sec. Yields are based on reacted acid.

†Calculated according to mole $CO_2 = K' \times$ number of coulombs passed.

Abbreviations used: HC = hydrocarbon; C = coulomb; decarb = decarboxylation; K = number of methylene groups in acid residue, $(CH_2)_K(COOH)_2$. C_KHC = hydrocarbons having C_K carbon atoms.

Comparison of the resutls obtained in the electrolysis of adipic, suberic, azelaic and sebacic acids

The results obtained with suberic and azelaic acid were compared with those previously obtained with adipic acid [3] and sebacic acid [4] under the same conditions (Table 4). The ratio of percent reacted acid to the coulombs passed was about the same for all the acids at 10.5×10^{-3}, except for suberic acid which was about 10% higher. This means that the same amount of coulombs was necessary to oxidize the same amount of acid. The higher efficiency of suberic acid is also reflected in the factor K' connecting CO_2 evolved with the current passed. Suberic acid had $K' = 5.6 \times 10^{-6}$ mol CO_2/coulomb while sebacic acid only 4.8×10^{-6} pointing to greater side oxidation of methanol in the latter. The extent of decarboxylation was about the same, except for sebacic acid which was a little lower, which indicates that the percent decarboxylation is not dependent on the coulombs passed or on the structure of the acid.

It can be seen from Fig. 1 that with adipic acid the yield in hydrocarbons is higher than in polymer unlike the other acids. With sebacic acid the ratio of the yields hydrocarbon/polymer was the lowest (Table 4) meaning that less dicarboxylic acid was wasted in side reactions of formation of hydrocarbon oligomers when the methylene chain length between the two carboxyl groups was increased.

Hydrocarbons having the same chain length were formed from the different acids, through different degrees of oligomerization. For example C_{24} hydrocarbons were formed from oligomerization of 6 molecules of adipic acid, 4 molecules of suberic acid and 3 molecules of sebacic acid. The compositions of these hydrocarbons obtained from the three acids were not the same. While the C_{24} n-alkane was 16% of the hydrocarbon fraction in all three acids, the yield of 1-alkene was the same only in the case of adipic and sebacic acids (40%) but lower with suberic acid (28%), and the yield of x-alkene was 38% with adipic acid, 32% with suberic and only 21% in the case sebacic acid. The yield of C_{24} cycloalkane increased from 5% in the case of adipic acid to 23% in the case of sebacic acid. This leads to the conclusion that the main factor governing the composition of the hydrocarbons having the same chain length is the number of molecules needed to condense together to form them. In fact if we compare the composition of C_{14} hydrocarbons obtained from 2 molecules of azelaic acid with the C_{16} hydrocarbons formed from 2 molecules of sebacic acid, we find that the compositions are similar [4]. It may be concluded further that, in the case of the different acids, it is not the same intermediates which lead to the formation of the hydrocarbons having the same chain length.

Differences were noticed in the methyl ester fraction. The yield went down from 3.6% for adipic acid to 2–2.3% for azelaic and sebacic acids. While with adipic acid the unsaturated esters were the major product (about 60–70%), with the other acids the saturated esters were the major product (55–65%). From adipic acid γ- and δ-lactones were obtained in relatively high yield while from the other acids, although the respective lactones were also formed, they were obtained in low yield.

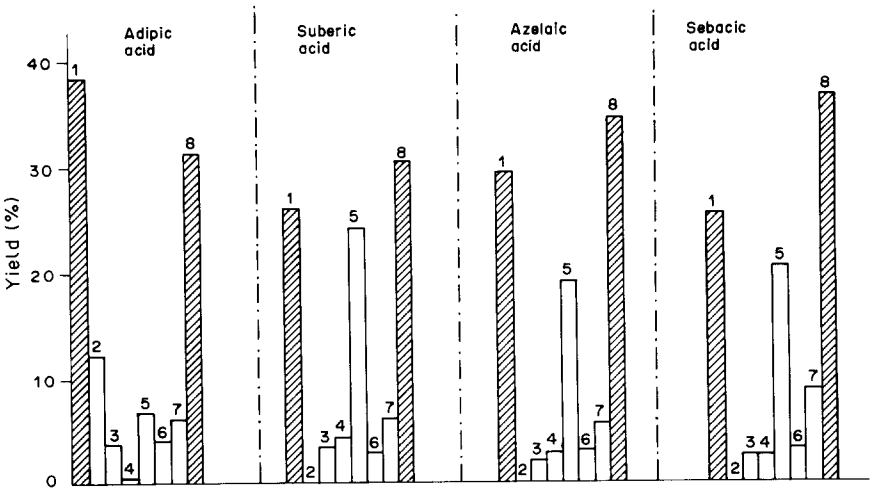


Fig. 1. Comparison of the yield of all products obtained in the electrolysis of various dicarboxylic acids in methanol:pyridine (1:1). (1) Hydrocarbons, (2) γ- and δ-valerolactone, (3) methyl esters, (4) methyl ethers, (5) carboxylic acids, (6) benzene fraction, (7) methanol fraction, (8) polymer.

The yield in methyl ethers was very low with adipic acid (0.35%) with suberic acid it was higher (4.2%) and went down to 2–2.5% with the others.

Comparison of the polymer fractions (Table 4) shows that the absolute yield in polymer was about the same except for sebacic acid which was a little higher. The extent of decarboxylation during polymer formation increases from 70% for adipic acid to 79% for sebacic acid, indicating that the hydrocarbon chain segments between the internal ester groups, increase in length on passing from adipic acid to sebacic acid, i.e. on increasing the number of methylene groups between the carboxyl groups of the diacids. All polymers were insoluble in organic solvents and infusible up to a temperature of 300°. The polymer from adipic acid was soluble in conc. H_2SO_4. However there are differences in structure of the various polymers. This is seen from the fact that the polymers after basic hydrolysis by KOH/ethylene glycol suffer different degrees of degradation. The polymer from adipic acid loses 32% in weight, that from suberic acid 21%, and from azelaic and sebacic acid only 14%. This result is in agreement with mmol ester groups/g polymer found in the polymers obtained from the four acids: 6.56 (adipic), 3.82 (suberic), 2.66 (azelaic) and 2.44 (sebacic). The polymers from azelaic and sebacic acids after being subjected to hydrolysis behaved like the starting polymers as regards solubility and infusibility up to 300°, while that from adipic acid suffered pronounced degradation and became soluble in organic solvents and melted at 90–95°. The polymer from suberic acid behaved in an intermediate manner.

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