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ELECTROCHEMICAL POLYMERIZATION OF DICARBOXYLIC ACIDS—III. QUANTITATIVE RESULTS IN THE ELECTROLYSIS OF ADIPIC ACID

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Abstract—The electrochemical polymerization of adipic acid via the Kolbe synthesis was investigated in methanol, methanol–pyridine and methanol–acetonitrile mixtures. The complex variety of products formed from C_4 and higher hydrocarbons, methyl esters, methyl ethers, lactones, oligomers and polymers in the various solvents were analyzed and compared. Generally the major products were the hydrocarbons and the polymers; the yield of the former decreased with increasing pyridine concentration and that of the latter increased.

INTRODUCTION

In Part I of this series [1] we showed, during study of the electrochemical polymerization of adipic acid that, besides the formation of insoluble polymer,

$$n\,HOOC(CH_2)_4COOH \xrightarrow[\text{oxidation}]{\text{electrolytic}} \{(CH_2)_4\}_n + 2n\,CO_2$$

there were oligomers and other low molecular weight fractions. In Part II [2] we separated and analyzed these products which included oligomeric, saturated and unsaturated hydrocarbons, mono- and dicarboxylic acids, γ- and δ-valerolactones, methyl ethers and methyl esters. In the present study we have studied quantitatively the effect of various solvents on the composition of the reaction products.

EXPERIMENTAL

The materials used, the electrolysis cell, the electrolysis of adipic acid, the determination of carboxylic acids by methylation, gas chromatography (GC) for the separation and quantitative determination of the various products by calibration curves were as described previously [2]. Column chromatography on silica gel was used to separate the higher oligomeric products into 4 fractions, viz. eluted by heptane, front-benzene, benzene and methanol as described before [2]. Triethylamine was used as a base. The initial current used in the electrolysis was 1.3 A, and its polarity was changed every 90 sec, so that the polymer formed peeled from the electrodes. The amount of current passing into the electrolysis cell was measured by a coulometer.

RESULTS AND DISCUSSION

The gases formed in the electrolysis of 4.38 g adipic acid (30 mmol) in the presence of triethylamine (3 mmol) in 30 ml solvent were collected either after prior passing through ascarite to trap the CO_2, or without trapping it. The gaseous products were analyzed by GC using a column of Porapack R. Nine peaks were obtained (Fig. 1) which were analyzed by GCMS and also by comparison with authentic samples and shown to be (1) N_2 (used as carrier gas in GC) and before it there was a peak belonging to H_2, (2) CO_2, (3) ethylene, (4) ethane, (5) formaldehyde, (6) methanol, (7, 8) C_4 hydrocarbons, (9) diethylamine. Reduction of the $Et_3\overset{+}{N}H$ cation during the electrolysis leads to the formation of ethylene, H_2 and diethylamine, and thus the amount of Et_3N becomes depleted. Formaldehyde is formed from oxidation of methanol.

Figure 2 shows that there is a direct relationship between the amount of gas evolved and the current passed and the proportionality factor, K, is 1.06×10^{-5} mol/l/C (calculated from line No. 5, Fig. 2). For CO_2 alone, the proportionality factor is 4.29×10^{-6} mol/l/C (calculated from line No. 2) indicating that the amount of CO_2 is less than half the amount of gases evolved.

The molar ratio of CO_2/H_2 obtained (Fig. 2) is 0.83, which is less than that required in the electrolysis of adipic acid whether it proceeds through a Kolbe mechanism where 2 mol CO_2 are evolved/mol H_2

$$n\,HOOC(CH_2)_4COOH \rightarrow {}^{\bullet}(CH_2)_4^{\bullet} + 2n\,CO_2 + n\,H_2$$

or through a cationic mechanism where it is 1:1, since a molecule of adipic acid loses only 1 CO_2 to produce a cation which reacts with a carboxylate group.

$$n\,HOOC(CH_2)_4COOH \rightarrow \{(CH_2)_4\text{–}COO\}_n + n\,H_2 + n\,CO_2$$

The excess H_2 is formed from a side reaction, viz. oxidation of methanol, which consumes part of the current passed.

On subtracting the amounts of CO_2 and H_2 evolved from the total gases, it can be calculated that in the experiment where 9034 C current were passed, the amount of C_4 hydrocarbons and ethylene evolved was 10.3 mmol. GC showed that it consisted of 7.38 mmol C_4 hydrocarbons and 1.95 mmol ethylene. Thus although 3 mmol Et_3N were used, only about 2/3 of it was reduced to yield ethylene and diethylamine.

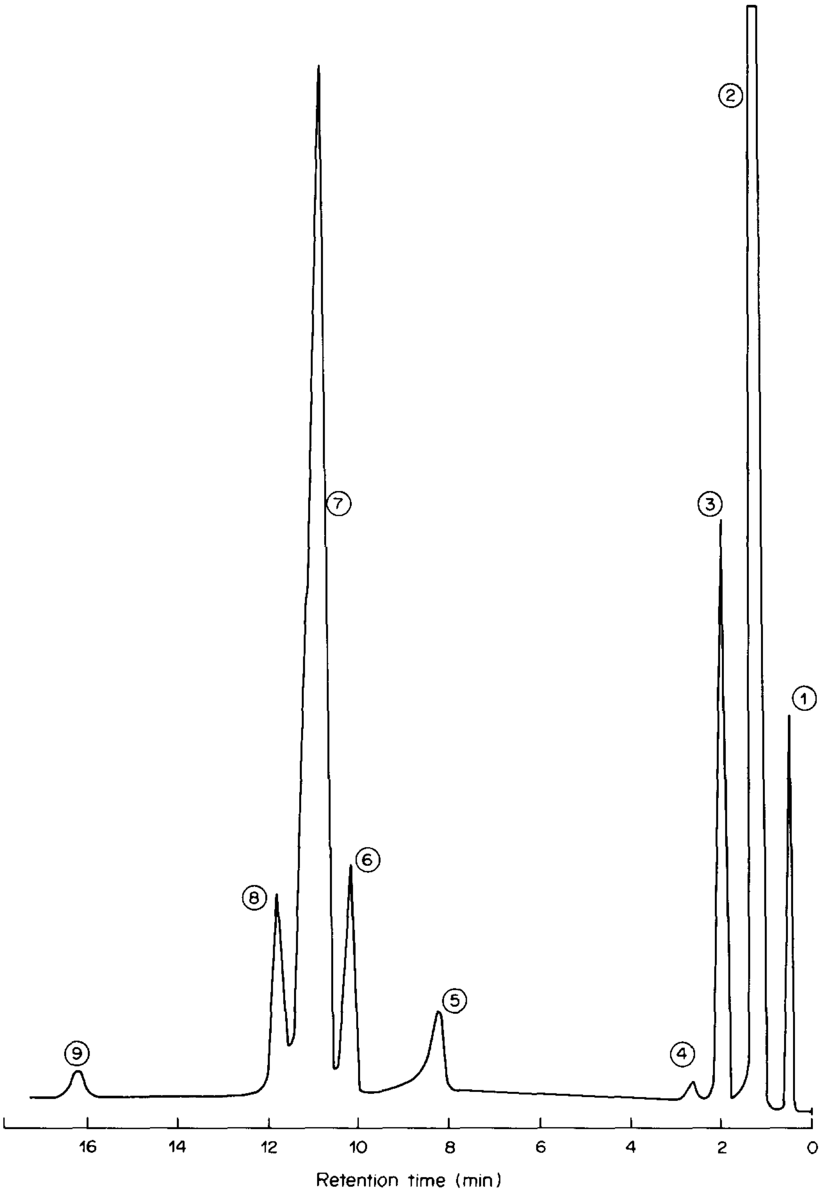

Fig. 1. GC separation of the gaseous fraction collected in electrolysis of adipic acid in methanol using a column of Porapak R, and temperature programming from 60° to 190°. (1) N_2, (2) CO_2, (3) ethylene, (4) ethane, (5) formaldehyde, (6) methanol, (7, 8) C_4-hydrocarbons, (9) diethylamine.

The C_4 hydrocarbon fraction collected in the gas system was analyzed by GC on a column of cinnamaldehyde [2] and was found to consist of 72% 1-butene, 14% *trans*-2-butene, 7% 1,3-butadiene, 4% *cis*-2-butene and 3% *n*-butane. The insoluble polymer obtained was filtered from the electrolysis solution and purified by refluxing benzene–methanol, yield 0.21 g.

The C_8 hydrocarbon fraction was determined by analysis of an aliquot portion of the solution by GC on a column of 20% squalane on C.P. [2]. The yield was 0.59 mmol, which consisted of 39% 1-octene, 28.5% *x*-octene (the place of the double bond is not known), 12.5% cyclo-octane, 11% 1,7-octadiene, and 9% *n*-octane. This C_8 hydrocarbon fraction was accompanied by two methyl esters of C_5 carboxylic acids: $CH_2{=}CH(CH_2)_2COOCH_3$ (0.07 mmol) and $CH_3(CH_2)_3COOCH_3$ (0.08 mmol).

Analysis of another aliquot from the electrolysis solution, by GC on a column of 5% butanediol succinate (BDS) on C.W., permitted the determination of C_{12} hydrocarbons (0.38 mmol) γ-valerolactone (1.87 mmol), δ-valerolactone (1.10 mmol) and two methyl esters of C_9 carboxylic acids $CH_3(CH_2)_7COOCH_3$ (0.08 mmol) and $CH_2{=}CH(CH_2)_6COOCH_3$ (0.16 mmol). The composition of the hydrocarbon fraction was 46.7% *x*-dodecene, 33.5% 1-dodecene, 12.4% cyclododecane and 7.4% *n*-dodecane.

Benzene and 5% KOH were added to the electrolysis solution, to divide the products into two phases. The carboxylic acid fraction was isolated by

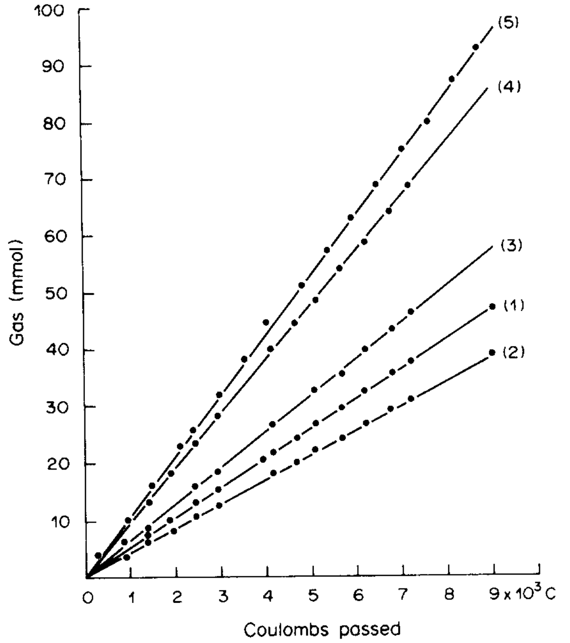

Fig. 2. Dependence of the quantity of gases evolved on the current passed in electrolysis of adipic acid in methanol. (1) H_2 (theoretical), (2) CO_2 collected on ascarite, (3) gases other than CO_2, (4) $CO_2 + H_2$, (5) gases collected including CO_2.

acidification of the aqueous solution with HCl, and extraction by ether. Methylation by diazomethane and GC on 5% BDS and on 3% SE 30 was used for the separation and quantitative determination of the acids. From the residue of adipic acid found, 78% of the starting acid were found to have reacted. The oligomeric carboxylic acids formed were (the amount of the material in mmol is given in brackets) C_9 acids: $CH_3(CH_2)_7COOH$ (0.06), $CH_2{=}CH(CH_2)_6COOH$ (0.18), C_{13} acids: $CH_3(CH_2)_{11}COOH$ (0.02), $CH_2{=}CH(CH_2)_{10}COOH$ (0.05), C_{17} acids: $CH_3(CH_2)_{15}COOH$ (0.014), $CH_2{=}CH(CH_2)_{14}COOH$ (0.021), dicarboxylic acids: sebacic $HOOC(CH_2)_8COOH$ (0.4), and $HOOC(CH_2)_{12}COOH$ (0.05).

The benzene phase from the KOH extract consisted of the non-acidic fraction; it was evaporated to dryness *in vacuo* and separated on silica gel to yield 4 fractions [2]; the heptane fraction (80 mg), the front benzene fraction (70 mg), the benzene fraction (140 mg) and the methanol fraction (80 mg).

The heptane fraction contained C_{12}–C_{32} oligomeric hydrocarbons as analyzed by GC on 3% SE 30 on C.W./H.M.D.S. The C_{12} hydrocarbons were determined straight from the electrolysis solution, while the lower C_8 hydrocarbons evaporated during the evaporation of the benzene-extract. The yields of the hydrocarbons were C_{12} (0.38 mmol, 60.8 molar % of the fraction), C_{16} (0.13 mmol, 20.8%, C_{20}(0.06 mmol, 9.6%), C_{24} (0.03 mmol, 4.8%), C_{28} (0.019 mmol, 2.9%) and C_{32} (0.007 mmol, 1.1%). Due to the relatively small amounts of C_{28} and C_{32} hydrocarbons, it was not possible to separate them. The lower hydrocarbon oligomers were separated as given in Table 1. It can be seen that the major fraction is always the unsaturated hydrocarbons. The proportion of the cyclic hydrocarbons decreases with increasing the ring size, probably due to smaller possibilities that the chain will assume a cyclic conformation necessary for cyclization.

The front benzene fraction contained no hydrocarbons and only methyl esters and methyl ethers which were separated by GC 3% SE 30 on C.W./H.M.D.S. The methyl esters were those derived from saturated straight chain carboxylic acids or from unsaturated acids having a terminal double bond, the latter being the major product (Table 2).

The yield of the esters decreases with increasing degree of oligomerization. With $n = 6$ (i.e. C_{24}) the molar fractional composition is only 0.9%, so that if higher oligomers are present they must be present in insignificant amounts.

Three types of oligomeric methyl ethers were formed:

(I) vinyl ethers $CH_3OCH(CH_3)(CH_2)_{4n-4}{-}CH{=}CH_2$

(II) saturated ethers $CH_3O(CH_2)_{4n-1}CH_3$

(III) unsaturated ethers with internal double bond $CH_3O(CH_2)_4CH{=}CH(CH_2)_{4n-7}{-}CH_3$

Table 1. Composition of the hydrocarbon fractions obtained in various solvents*

Hydrocarbon	*n*-Alkane, (%)	1-Alkene, (%)	*x*-Alkene, (%)	Cycloalkane, (%)
C_4	3; 7; 10	72; 62; 60	18; 25; 23	7; 6; 7
	10; 31	58; 46	24; 20	8; 2†
C_8‡	9; 12; 8;	39; 33; 45	29; 28; 27;	12; 17; 11
	10; 19	30; 27	25; 21	24; 20
C_{12}	7; 13; 8	34; 35; 34	47; 39; 47	12; 13; 11
	13; 27	43; 41	30; 27	14; 5
C_{16}	18; 13; 19	38; 37; 39	38; 44; 36	6; 6; 6
	25; 26	41; 42	30; 26	4; 6
C_{20}	17; 13; 19	38; 39; 39	43; 44; 36	2; 4; 6
	28; 0	43; 0	25; 0	4; 0
C_{24}	19; 13; 16	38; 39; 41	40; 42; 38	3; 6; 5
	21; 0	45; 0	29; 0	5; 0

*Experimental conditions as in Table 7. The results given under the various headings belong to the different solvents in the following order: methanol; M:P (1:4); M:P (1:1) given in 1st row followed in the 2nd row by the results of M:A (1:1) followed by M:P (1:4). The percentage yield given under every product is that of the respective product out of the total hydrocarbon oligomers having the same *n* obtained in one of the solvents mentioned.

†The product with the C_4 hydrocarbons is 1,3-butadiene.

‡In the C_8-hydrocarbon fraction 1,7-octadienes were also present, their percentages (in the order of the solvents mentioned above) were: 11; 10; 9; 11; 13.

Table 2. Balance of the products obtained in the electrolysis of adipic acid in methanol*

$(CH_2)_{4n}$—X	Hydrocarbons		Methyl esters		Methyl ethers		Carboxylic acids		Adipic acid
n =	mmol	(%)	mmol	(%)	mmol	(%)	mmol	(%)	(%)
1	7.38	(32.1)	3.12	(13.5)†	0.34	(1.5)	0	(0)	47.1
2	0.49	(4.2)	0.24	(1.2)	0.15	(1.3)	0.64	(5.6)	12.3
3	0.38	(5.0)	0.04	(0.5)	0.06	(0.8)	0.12	(1.6)	7.9
4	0.13	(2.3)	0.02	(0.4)	0.04	(0.7)	0.035	(0.6)	4.0
5	0.06	(1.3)	0.01	(0.2)	0.02	(0.5)	0	(0)	2.0
6	0.03	(0.8)	0.003	(0.1)	0.01	(0.3)	0	(0)	1.2
7	0.018	(0.5)	0	(0)	0.003	(0.1)	0	(0)	0.6
8	0.007	(0.25)	0	(0)	0	(0)	0	(0)	0.25
		(46.5)‡		(15.9)‡		(5.2)‡		(7.8)‡	
					Benzene, fraction, yield				6.4
					Methanol, fraction, yield				3.2
					Polymer, yield				10.0
				Total yield of recovered products§					94.95%

*Experimental conditions as in Table 1; 77% of the adipic acid reacted. The percentage given under each product is that of the reacted adipic acid that was converted into that product. The last column gives the percent of adipic acid converted to products having the same n (degree of oligomerization). The structure of the products was taken as $(CH_2)_{4n}$ for the hydrocarbons, $(CH_2)_{4n}COOCH_3$ for the methyl esters, $(CH_2)_{4n}OCH_3$ for the methyl ethers, and $(CH_2)_{4n}COOH$ and/or $HOOC(CH_2)_4COOH$ for the carboxylic acids.

†Composed of methyl valerate (0.15 mmol) and γ- and δ-valerolactone (2.97 mmol).

‡Total yield of that type of product.

§Does not include 14.7 mg of unidentified products from the front-benzene fraction.

The quantity of methyl ethers (**I** + **II**) is about 2–2.5 times greater than that of ether **III**. For the ether having $n = 3$, it was possible to determine separately each of the three components by GC using a BDS column which gives better resolution than the SE 30 [2] and the results were **I** 43.2%, **II** 26.4% and **III** 30.4%, meaning that the unsaturated ethers were 3 times as much as the saturated one.

About 20% of the front-benzene fraction could not be identified by GCMS. In i.r. and NMR of the whole fraction, there were no new groups other than those belonging to the materials determined, so that it can be that they are mainly materials isomeric to those already identified.

The benzene fraction did not have any volatile material in GC, because it is composed of oligomers of relatively high molecular weight. The oxygen content in this fraction is higher than in the front-benzene one, due to an increase in the ether and methyl ester groups as well as to the presence of internal ester and γ-lactone groups. Evidence for the structure of the oligomers was obtained from i.r., NMR and elemental analysis. The structure of the products was described previously [2]. The extent of decarboxylation in this fraction was 88.5% (pure Kolbe reaction leads to 100% decarboxylation).

The methanol fraction consisted of oligomers with a still higher oxygen content, that were not volatile and the extent of decarboxylation was lower, 70%. Their structure was previously described [2].

In conclusion the electrolysis of adipic acid in methanol leads to the formation of a variety of products from gaseous products to polymers. The products may be presented by the general formula $(CH_2)_n$—X where X is a functional group. Based on this structure, we can compare the electrolysis reaction to a polymerization where oligomers are formed having varied molecular weights. The loss of a carboxyl group in the electrolysis and its conversion to a stable group, such as methyl ester, that cannot undergo further oxidation, is reminiscent of termination reactions in free radical polymerizations of vinyl monomers.

A summary of the results of the electrolysis in methanol is given in Table 2. The last column of the table shows the percent of reacted adipic acid that was converted to different products having the same degree of polymerization. The percentages given in the other columns refer to the adipic acid consumed in the formation of the specific products. It is seen that the percent of reacted adipic acid converted to $(CH_2)_{4n}$—X products goes down exponentially from $n = 1$ (47.2%) to $n = 8$ (0.24%).

In the $n = 1$ fraction, the C_4 hydrocarbon fraction is the major one (32%) followed by that of γ- and δ-valerolactone (12.9%). The total yield in methyl esters of all the oligomeric products of this type was 4%, that of the methyl ethers was 5.2% while that of the acids was 7.5%.

The amount of CO_2 liberated was 38.77 mmol. Since 23 mmol adipic acid reacted, then for 100% decarboxylation 46 mmol CO_2 should have been liberated. This shows that the overall % of decarboxylation that occurred was 84.3%.

From measurements of the current passed in the electrolysis cell, it was seen that 9034 C were needed for the oxidation of 23 mmol adipic acid. Actually only 4439 C should have been required according to the Kolbe mechanism.

$$HOOC(CH_2)_4COOH \rightarrow \text{-}(CH_2\text{-})_4 + 2CO_2 + 2H^+ + 2e^-$$

This means that approximately $4e^-$ were needed for the oxidation instead of the theoretical $2e^-$ needed for the oxidation of 1 mol adipic acid. This discrepancy is due to current wasted on the side reaction, viz. oxidation of methanol.

Study of other solvents for the electrolysis

The following solvent mixtures were studied in detail as described for methanol:

(1) Methanol:pyridine (M:P) (1:1)
(2) Methanol:acetonitrile (M:A) (1:1)
(3) Methanol:pyridine (4:1)
(4) Methanol:pyridine (1:4)

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

$(CH_2)_{4n}$—X n =	Hydrocarbons mmol	 (%)	Methyl esters mmol	 (%)	Carboxylic acids mmol	 (%)	Adipic acid (%)
1	6.56	(24.5)	3.34	(12.4)†	0	(0)	36.9
2	0.62	(4.6)	0.2	(1.5)‡	0.52	(3.9)	10.0
3	0.53	(6.0)	0.07	(0.7)§	0.21	(2.3)	9.0
4	0.10	(1.5)	0.025	(0.4)	0.05	(0.7)	2.6
5	0.04	(0.7)	0.015	(0.3)	0	(0)	1.0
6	0.02	(0.48)	0.005	(0.12)	0	(0)	0.6
7	0.01	(0.26)	0	(0)	0	(0)	0.26
8	0.004	(0.01)	0	(0)	0	(0)	0.01
		38.05		15.4		6.9	
				Benzene fraction, yield			4.0
				Methanol fraction, yield			6.2
				polymer, yield			31.0
				Total yield of recovered products			101.6

*Electrolysis carried out as in Table 1 using 30 ml of methanol:pyridine (1:1 by volume); 89% of the adipic acid reacted. Yields based on reacted adipic acid. See Table 2 for explanation of the headings.

†Composed of methyl valerate (0.12 mmol) and γ- and δ-valerolactones (3.22 mmol).

‡Includes 0.07 mmol of a C_9-γ-lactone and dimethyl sebacate.

§Includes 0.03 mmol of C_{12} methyl ether.

When pyridine was used alone as a solvent with Et_3N as a base, the current that could be passed was small, and went down to zero during the electrolysis as the electrodes became coated with a brown polymer film, that did not separate from the electrode even on changing the direction of the current. However, when the pyridine was diluted with methanol, it was possible to pass a stronger current through the solution. At M:P (1:4), it was still difficult to pass more than 0.3 A (0.05 A/cm^2 of electrode surface) due to resistance of the solution but at M:P (1:1) it was possible to pass 1.3 A (0.22 A/cm^2). Although usually current densities of 0.25–1.0 A/cm^2 are used in the Kolbe reaction [3], we decided to work at lower current densities, due to technical problems. Increasing the current leads to more heat evolution with consequently greater evaporation of the methanol, which may interfere in the determination of the gaseous products. The electrolysis was stopped after several hours, when the current dropped to about 0.8 A. Similarly, when acetonitrile alone was used as solvent, the current that passed was very weak, due to the low solubility of adipic acid in the solvent, and fell rapidly to zero. However it was possible to carry out the electrolysis in a mixture of M:A (1:1).

A summary of the results obtained in the various solvent mixtures is given in Tables 3–6. In all the experiments in the various solvents, the molar amount of the gaseous fractions collected was directly proportional to the number of coulombs passed. Table 7 gives a summary of the factor that connects the moles of CO_2 evolved with the number of coulombs passed, together with the percentage of decarboxylation. Excluding the case of M:P (1:4) where the current passed was much lower than with the other solvents, the percent decarboxylation in all the solvents was about 82% based on reacted adipic acid. Based on the fact that the percent of reacted adipic

Table 4. Balance of the products obtained in the electrolysis of adipic acid in methanol:acetonitrile (1:1)*

$(CH_2)_{4n}$—X n =	Hydrocarbons mmol	 (%)	Methyl esters mmol	 (%)	Methyl ethers mmol	 (%)	Carboxylic acids mmol	 (%)	Adipic acid (%)
1	7.18	(25.0)	2.98	(10.0)†	0.22	(0.8)	0	(0)	35.8
2	1.60	(11.0)	0.44	(3.0)‡	0.07	(0.5)	0.43	(3.0)	17.5
3	0.21	(2.2)	0.06	(0.6)	0.03	(0.3)	0.08	(0.9)	4.0
4	0.076	(1.1)	0.03	(0.4)	0.02	(0.3)	0.01	(0.1)	1.9
5	0.032	(0.5)	0.015	(0.3)	0	(0)	0	(0)	0.8
6	0.018	(0.36)	0.007	(0.14)	0	(0)	0	(0)	0.5
7	0.013	(0.3)	0	(0)	0	(0)	0	(0)	0.3
8	0.01	(0.27)	0	(0)	0	(0)	0	(0)	0.27
		40.7		14.4		1.9		4.0	
						Benzene fraction, yield			4.2
						Methanol fraction, yield			9.0
						Polymer, yield			22.0
						Total yield of recovered products§			96.3

*Electrolysis carried out as in Table 1 using 30 ml of methanol:acetonitrile (1:1); 97% of the adipic acid reacted. See Table 2 for explanation of the headings.

†Composed of methyl valerate (0.42 mmol), dimethyl adipate (0.04 mmol), and γ- and δ-valerolactones (2.52 mmol).

‡Composed of methyl ester of C_9 carboxylic acid (0.39 mmol) and dimethyl sebacate (0.05 mmol).

§Does not include 10.8 mg of unidentified products from the front benzene fraction.

Table 5. Balance of the products obtained in the electrolysis of adipic acid in methanol:pyridine (4:1)*

$(CH_2)_{4n}$—X	Hydrocarbons		Methyl esters		Methyl ethers		Carboxylic acids		Adipic acid
n =	mmol	(%)	mmol	(%)	mmol	(%)	mmol	(%)	(%)
1	7.39	(30.0)	1.66	(6.9)†	0.23	(0.9)	0	(0)	37.8
2	0.79	(6.4)	0.10	(0.8)	0.10	(0.8)	0.84	(6.8)	14.8
3	0.36	(4.4)	0.04	(0.5)	0.08	(1.0)	0.64	(7.8)	13.7
4	0.13	(2.1)	0.02	(0.3)	0.04	(0.6)	0.09	(1.4)	4.4
5	0.06	(1.2)	0.014	(0.3)	0.02	(0.4)	0.03	(0.5)	2.4
6	0.03	(0.8)	0.004	(0.1)	0.014	(0.3)	0	(0)	1.2
7	0.013	(0.4)	0.002	(0.05)	0.002	(0.05)	0	(0)	0.5
8	0.004	(0.1)	0	(0)	0	(0)	0	(0)	0.1
		45.3		9.0		4.1		16.5	
					Benzene fraction, yield				2.3
					Methanol fraction, yield				6.0
					Polymer, yield				17.0
				Total yield of recovered products					100.2

*Electrolysis carried out as in Table 1 using 30 ml of methanol:pyridine (4:1); 82% of the adipic acid reacted. Yields are based on reacted adipic acid. See Table 2 for explanation of the headings.

†Composed of methyl valerate (0.21 mmol) and γ- and δ-valerolactones (1.45 mmol).

Table 6. Balance of the products obtained in the electrolysis of adipic acid in methanol:pyridine (1:4)*

$(CH_2)_{4n}$—X	Hydrocarbons		Methyl esters		Carboxylic acids		Adipic acid
n =	mmol	(%)	mmol	(%)	mmol	(%)	(%)
1	2.96	(18.0)	0.95	(5.9)†	1.19	(7.4)‡	31.3
2	0.13	(1.6)	0.09	(1.1)	1.09	(13.6)	16.3
3	0.09	(1.7)	0.03	(0.6)	0	(0)	2.3
4	0.026	(0.6)	0.027	(0.7)§	0	(0)	1.3
5	0.01	(0.3)	0	(0)	0	(0)	0.3
		22.2		8.3		21.0	
			Benzene and Methanol fraction, yield				6.6
			Polymer yield				39.0
							97.1

*Reaction conditions as in Table 1 using 30 ml of methanol:pyridine (1:4); 54% of the adipic acid reacted. The current passed was only 0.3 A due to resistance of the solution. See Table 2 for explanation of the headings.

†Composed of methyl valerate (0.29 mmol) and γ- and δ-valerolactone (0.66 mmol).

‡The C_5 acids were valeric acid (26%) and the unsaturated acid $CH_2{=}CHCH_2CH_2COOH$ (74%).

§Composed of C_{17} methyl esters (0.007 mmol) and C_{16} methyl ethers (0.02 mmol).

acid was not the same in all the reactions, this means that the percent decarboxylation is not dependent on reaction yield, within the limits investigated.

The overall extent of decarboxylation in the reaction was between about 70% that of the polymer to 100% that of hydrocarbon formation, except in the case of M:P (1:4) where the overall percent decarboxylation was 65% i.e. close to that of the polymer percent decarboxylation of 61%. This is due to the difference in the distribution of the products. In the case of M:P (1:4) (Table 6) the major products were polymer (37%), hydrocarbons (23%), acids (21%) and esters (8%); the acidic fraction was composed of valeric acid (50% decarboxylation) and sebacic acid (50% decarboxylation). Based on these major fractions, it is possible to calculate the percent decarboxylation:

$$\frac{(37 \times 61) + (23 \times 100) + (21 \times 50) + (8 \times 50)}{(37 + 23 + 21 + 8)} = 67\%$$

This is close to the 65% calculated from measurement of CO_2 evolved.

Table 7. Gaseous products in the polymerization of adipic acid in various solvents*

Solvent	Coulombs passed	Adipic acid reacted, %	$K(CO_2)$ (C/mol $\times 10^{-6}$)	K' (gases-CO_2) (C/mol $\times 10^{-6}$)	Decarboxylation (%)	Ethylene (mmol)
Methanol	9034	77	4.3	6.3	84	1.95
M:P (4:1)	6611	82	6.1	6.6	83	1.94
M:P (1:1)	8536	89	5.1	6.2	81	2.12
M:A (1:1)	8950	97	5.2	6.2	81	2.32
M:P (1:4)	4431	54	4.7	5.8	65	0.51

*Adipic acid (4.38 g, 30 mmol) was dissolved in 30 ml solvent, Et_3N (3 mmol) was added and the electrolysis carried out for several hours at 1.3 A except for M:P (1:4) where it was 0.3 A.

K and K' are constants connecting the amount of CO_2 and the amount of gases less that of the CO_2, respectively with the current passed, given in C/mol gas generated.

The constant, K, connecting the amount of CO_2 evolved with the coulombs passed is highest in the case of M:P (4:1) (6.1×10^{-6} mmol CO_2/coulomb) (Table 7) meaning that, in this solvent mixture, the amount of CO_2 evolved, for the same amount of coulombs, is the highest. This is due to higher yields of hydrocarbons in this solvent. For methanol, K was the lowest (4.3×10^{-6}). This is because in pure methanol, there is more side reaction of methanol oxidation. The hydrocarbon yields in M:P (4:1) (Table 5) and in methanol (Table 2) are about the same, meaning that the presence of 20% pyridine in the mixture suppresses the methanol oxidation.

When the fraction of pyridine in the solvent mixture increased, there was an increase in polymer yield. The extent of decarboxylation during polymer formation was about 70%, which is lower than that of hydrocarbon formation (100%). This is due to the participation of the cationic mechanism which requires $2e^-$ for the evolution of 1 mole CO_2, while the radical (Kolbe) mechanism requires only $1e^-$.

$$\mathrm{HOOC(CH_2)_3CH_2COO^-} \xrightarrow{-e^-} \mathrm{HCOO(CH_2)_3CH_2^{\cdot}}$$

$$+\mathrm{CO_2} \xrightarrow{-e} \mathrm{HCOO(CH_2)_3CH_2^+}$$

Therefore with increasing polymer formation, there is increase in the amount of current required for the evolution of the same amount of CO_2. That is why the value of the constant, K, decreased on increasing the pyridine concentration in the solvent mixture.

The constant, K', connecting gases evolved other than CO_2 with the current passed, shows only small changes with the solvent.

As regards the amount of ethylene evolved from oxidation of the Et_3N, it is seen that, except for the case of M:P (1:4) where it is low, the results with the other solvents are about the same (Table 7). This can be due to participation of the pyridine as a base, besides Et_3N, at the higher concentrations.

It is interesting that, in the two solvent mixtures M:P (1:1) and M:A (1:1), the composition of the gaseous products of the electrolysis is essentially the same (Table 7) in spite of the differences between the solvents: pyridine is basic and has a dielectric constant of 13 while acetonitrile is neutral and has a dielectric constant of 37.5.

The yield of the C_4-hydrocarbons decreased with increasing the pyridine fraction in the solvent mixture (Tables 2–6). Experiments were carried out with the two "extreme" solvent mixtures M:P (4:1) and M:P (1:4) in which the composition of the hydrocarbons was determined as a function of the coulombs passed. No change in composition was noticed during the electrolysis. The composition of the C_4-hydrocarbons was studied as a function of the solvent (Table 1). In the three solvent mixtures M:P (4:1), M:P (1:1) and M:A (1:1), the composition of the hydrocarbons was similar and characterized by a high percentage (82–87%) of the unsaturated products, 1-butene and 2-butenes. In methanol it was still higher (90%) but in M:P (1:4) it was much lower (66%) accompanied by a large increase in the n-butane fraction (31%), indicating that an increase in pyridine leads to an increase in the saturated fraction.

In all cases the C_4 hydrocarbons constitute most of the hydrocarbon fractions (61–78%), and the yield of the hydrocarbons decreases sharply with increasing degree of oligomerization. No hydrocarbons having $n > 8$ were found. In M:P (1:4) only hydrocarbons up to $n = 5$ were formed, perhaps because of the greater tendency for polymer formation in this solvent mixture.

The hydrocarbons formed belong to four groups: linear saturated; linear unsaturated with a terminal C=C double bond; unsaturated with an internal double bond having a *trans* configuration (x-alkene) and cyclic hydrocarbons. Table 1 summarizes the composition of the hydrocarbon oligomers obtained in the various solvents. In the C_8 fractions, 1,7-octadienes were also formed in all the solvents, at about 10% yield. The unsaturated 1-alkenes and x-alkenes form most (70–80%) of the products. In

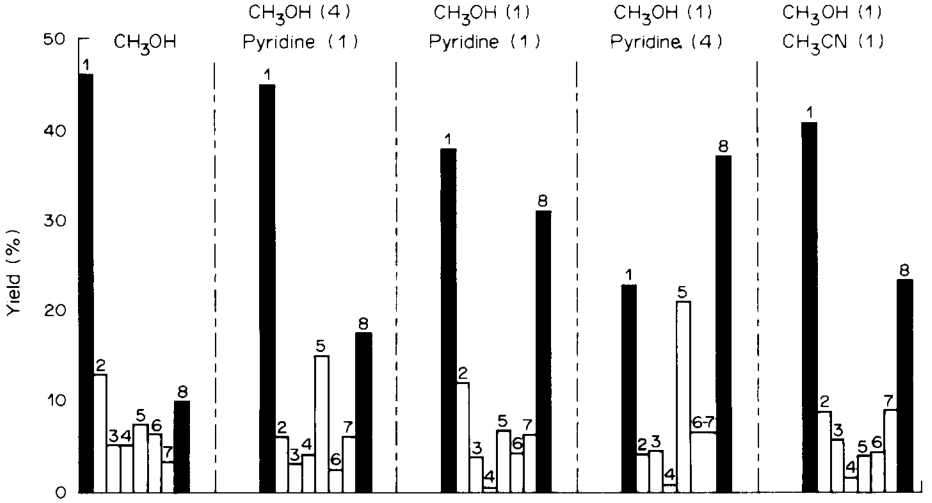

Fig. 3. Comparison of the yield of all the products obtained in electrolysis of adipic acid in various solvents. (1) Hydrocarbons, (2) γ- and δ-valerolactone, (3) methyl esters, (4) methyl ethers, (5) carboxylic acids, (6) benzene fraction, (7) methanol fraction, (8) polymer.

M:P (1:4), their quantity is lower and that of the *n*-alkanes is higher.

Figure 3 gives the yields of the products obtained in the various solvents. Generally the major products are the hydrocarbons and the polymer; the yield of the former decreased with increasing pyridine concentration and that of the latter increased. The yield of the hydrocarbons decreased from 46% in methanol to 23% in M:P (1:4). This cannot be due to the fact that in the latter solvent mixture only 4431 coulombs were passed compared to about 9000 coulombs in most of the other solvents, since we have shown that there is no change in the composition of the products during the electrolysis, i.e. no dependence of the composition on the amount of current passed. It can be assumed that, on increasing the pyridine concentration, there is an increase in the participation of the cationic mechanism yielding products having a higher percentage of oxygen. Generally the solvent has a large effect on the yield of the hydrocarbons but a smaller effect on their composition (Table 1).

γ- and δ-valerolactones. The lactones were formed in relatively high yield between 12–13% in methanol or M:P (1:1) (Fig. 3) and their yield decreased to 4% in M:P (1:4). The ratio between the two was approximately $\gamma:\delta$ (2:1) except in M:A (1:1) where it was 6:1. In general the products in which $n = 1$ (C_4-hydrocarbons and valerolactones) constitute a high proportion of the different products formed in the electrolysis.

Methyl esters. The yield in all the solvents was between 4–6% (Fig. 3). The yield of higher oligomers decreased with increasing *n*. Thus oligomeric methyl esters up to $n = 7$ were found in methanol or M:P (4:1), up to $n = 6$ in M:P (1:1) or M:A (1:1) and up to $n = 4$ in M:P (1:4). The methyl esters belong to both saturated and vinyl unsaturated acids. The unsaturated ester in many of the cases was about twice as much as the saturated. In M:P (1:4) there was however about 90% of the saturated ester of $n = 1$. We have noticed before that in this solvent mixture there is an increase in the formation of saturated products. In M:A (1:1) with $n > 3$, the amounts of saturated and unsaturated esters were about the same. In M:P (1:1), dimethyl sebacate and a C_9-γ-lactone were found. The formation of the latter compound is important since there is evidence for the presence of γ-lactone structures in the oligomers present in the benzene fraction.

Methyl ethers. The yield of methyl ethers was dependent on the composition of the solvent (Fig. 3). In methanol it was 5%, in M:P (4:1) 4% and decreased to 0.3–0.5% in solvent mixtures having a higher fraction of pyridine, due to suppression of methyl ether formation in this solvent. In fact in M:P (1:1) only a C_{12} methyl ether was found. The yield of methyl ethers in M:A (1:1) was low (1.4%) and oligomeric ethers from $n = 1$ to $n = 4$ were found.

Carboxylic acids. Both saturated and unsaturated acids having a terminal double bond were formed (Fig. 3). For C_9 and C_{13} acids, the unsaturated acids were between 69–78% of the total, while for the C_{17} acids they were only 60–63%, due to an increase in the saturated fraction. In M:P (1:4) the saturated acids constituted the major fraction (75%). It may be

Table 8. Effect of solvent on the highest oligomeric fractions and polymer*

	Benzene fraction					Methanol fraction					Polymer	
Solvent	Yield (%)	Decarboxylation (%)	CH_2/X ratio	General formula	Structure	Yield (%)	Decarboxylation (%)	CH_2/X ratio	General formula	Structure	Yield (%)	Decarboxylation (%)
Methanol	8.6	88.5	10.4	$C_{57}H_{109}O_7$	$(A)_{13}(COO)_3$	3.6	70	5.0	$C_{51}H_{98}O_{15}$	$(A)_{10}(COO)_6$	10	78
M:P (4:1)	2.3	89	10.4	$C_{57}H_{108}O_7$	$(A)_{14}(COO)_3$	6.0	75	4.8	$C_{29}H_{55}O_7$	$(A)_6(COO)_3$	17	77
M:P (1:1)	4.0	83	8.0	$C_{91}H_{171}O_{15}$	$(A)_{20}(COO)_7$	6.0	74	4.8	$C_{48}H_{85}O_{11}$	$(A)_{9.5}(COO)_5$	31	70
M:A (1:1)	4.0	89	9.0	$C_{58}H_{109}O_7$	$(A)_{13.5}(COO)_3$	9.0	81	5.6	$C_{74}H_{142}O_{15}N$	$(A)_{16}(COO)_6$	22	70
M:P (1:4)†	7.0	69	4.0	$C_{68}H_{116}O_{17}N$	$(A)_{13}(COO)_8$	—	—	—			39	61

*Experimental conditions as in Table 7. The benzene and methanol fractions are composed of oligomers which are not volatile in GC. The percent decarboxylation calculated from composition of the fractions. The CH_2/X ratio shows the average number of methylene groups/functional or terminal group (X). The general formula of the oligomeric fractions was determined from NMR. The structure of the oligomers is based on subtracting from the general formula the groups that do not originate from adipic acid such as methoxy etc. (A) stands for $-(CH_2)_4-$ the methylene residues from adipic acid.

†Due to their small quantities the benzene and methanol fractions were combined and analyzed.

noted that the carboxylic acids formed during the electrolysis may participate in the electrolysis and undergo oxidation. However, due to the high concentration of adipic acid, their participation may become significant only towards the end of the reaction.

Benzene fraction. The yield of this fraction was 8.6% in methanol and decreased to 4% in M:P (1:1) or M:A (1:1) (Table 8). The structure of these fractions was studied by i.r. and NMR as described previously [2]. By NMR, the number of CH_2 groups was determined, as well as other groups such as CH_3, methoxy, ester etc. and a general formula was deduced. On subtracting from this formula the groups that did not originate from adipic acid, a structural formula was written composed of adipic acid residues [2] and from this the percent decarboxylation was calculated.

Methanol fraction. The yield of this fraction increased from 3.6% in methanol to 9% in M:A (1:1) (Table 8). However the percent decarboxylation and the ratio of methylene groups to functional or terminal groups (CH_2/X) was quite similar in methanol, M:P (4:1) and M:P (1:1) indicating that their structures are similar.

Polymer. The polymer is a major product and its yield increased with increasing the pyridine fraction in the solvent (Table 8). The percent decarboxylation leading to the polymer structure obtained in methanol was 78% and went down to 61% for M:P (1:4). This means that the polymer obtained in methanol had a greater hydrocarbon structure than that obtained in M:P. Other details about the polymers were reported previously [1].

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