

way.¹⁶ The concentration of alkoxide was taken as the difference between the two values. Dissolved water causes a low value to be obtained, but the error is small in the systems described above.

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Anodic Oxidation of Aliphatic Acids at Carbon Anodes

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Electrolysis of simple aliphatic acids at carbon anodes produced high yields of products for which carbonium ion like species are intermediates: from acetic acid, methyl acetate was formed in 82% yield; from butyric acid, propene and cyclopropane in 1:2 ratio and *n*- and isopropyl butyrate also in 1:2 ratio. Pentanoic, 2-methylbutyric, and 3-methylbutyric acids yielded nearly all the possible butenes and butyl esters in addition to methylcyclopropane. These products are compared with the products of other carbonium ion reactions.

Introduction

Anodic oxidation—Kolbe electrolysis—of carboxylic acids produces hydrocarbons through a free radical sequence, $\text{RCOO}^- \rightarrow \text{RCOO}\cdot \rightarrow \text{R}\cdot + \text{CO}_2$, $2\text{R}\cdot \rightarrow \text{R-R}$.¹ In many cases, especially with α -substituted carboxylic acids, abnormal products such as olefins, alcohols, ethers, and esters are obtained which are more typical of carbonium ion reactions. Some specific examples are the formation of di- and triphenylmethyl ethers and acetates by electrolysis of di- and triphenylacetic acids in methanol or acetic acid,^{2a} and of *N*-methoxymethyl amides by electrolysis of acylaminoacetic acids in methanol at platinum electrodes.^{2b}

That cationic intermediates can be involved in such anodic oxidations was shown by Corey and co-workers³ who compared the products of some solvolysis reactions and anodic oxidations. For example, anodic oxidation of *exo*- or *endo*-norbornane-2-carboxylic acid in methanol at platinum electrodes gave *exo*-norbornyl methyl ether, and *exo*- or *endo*-5-norbornene-2-carboxylic acid gave 3-methoxynortricyclene. Electrolysis of cyclobutanecarboxylic acid in water and deamination of cyclobutylamine both gave the same mixture of cyclobutanol, cyclopropylcarbinol, and allylcarbinol. The same anodic oxidation mechanism was invoked to explain the olefin and ether obtained by electrolysis in alcohols of $\beta\beta$ -acetoxybisnorallocholic acid—an α -methyl-substituted acid.⁴ In a system without α -substituents—3,3-diphenylpropanoic acid—Bonner and Mango have shown that electrolysis causes 1,2-phenyl migration *via* 2,2-diphenylethylcarbonium ion.⁵

In these and many other examples of the failure of the normal Kolbe electrolysis to occur the carbonium ion intermediates which might be generated from the initially formed alkyl radicals are relatively stable. With simple aliphatic carboxylic acids, particularly those with no α -substituents, the case for carbonium

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ion formation is less clear. Here, the abnormal (non-Kolbe) products are formed in minor amounts at platinum anodes while the radical-coupling reaction is the predominant reaction. We have found that at *carbon anodes* simple aliphatic acids yield the abnormal products almost exclusively. We have compared these products with those of the carbonium ion reactions, deamination⁶ and deoxidation.⁷

Experimental

Apparatus.—Cell A consisted of a 1-l. resin kettle fitted with a stirrer, thermometer, reflux condenser, cooling bath, and an electrode assembly. The electrode assembly was made of four $1 \times 32 \times 115$ mm. copper plates and three $6.5 \times 32 \times 115$ mm. carbon plates which were stacked alternately and held together by two Teflon⁸ rods which passed through all seven pieces. Teflon washers on the rods maintained 4 mm. spaces between the plates. This assembly was mounted vertically in the cell. The carbon plates were connected together as the anode and the copper plates were connected together as the cathode. The carbon plates were cut from the materials described in Table I.

TABLE I
ANODE CARBON

	Manufacturer	Apparent density, g./cc.	Real density, g./cc.	Pore volume, cc./g.
KC	Unknown	1.70	2.10	0.110
HPL	Great Lakes Carbon	1.68	2.24	.149
TPL	Great Lakes Carbon	1.78	2.24	.118
NC60	National Carbon	1.05	..	.457

Cell B was a 3.0-cm. diameter glass cylinder of about 100-ml. capacity fitted with a reflux condenser, thermometer, magnetic stirrer, and two 1.5×3.6 cm. platinum foil electrodes mounted parallel and 0.6 cm. apart.

The power supply was a variable transformer and rectifier capable of providing a direct current of 0 to 5 amp. at 0 to 120 v.

Analytical Methods.—Gas analyses were obtained by a combination of gas chromatographic and mass spectrometric methods. The relative amounts of propene, cyclopropane, and C_4H_8 and C_4H_{10} isomers were determined by gas chromatography on a 50 ft. column of di-*n*-propyl sulfone and dimethyl sulfolane on Chromosorb.⁹ Absolute amounts of hydrogen, carbon dioxide, other light gases, and total C_4H_8 compounds were determined mass spectrometrically. Cyclopropane and propene from the

(1) For a review of the Kolbe electrosynthesis see: (a) B. C. L. Weedon in R. A. Raphael, E. C. Taylor, and H. Wynberg, "Advances in Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, Vol. 1, pp. 1-34; (b) G. E. Svadkovskaya and S. A. Voitkevich, *Russ. Chem. Rev. Eng. Trans.*, **29**, 161 (1960); (c) B. C. L. Weedon, *Quart. Rev. (London)*, **6**, 380 (1952).

(2) (a) R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, *J. Chem. Soc.*, 3641 (1952); (b) *ibid.*, 2854 (1951).

(3) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960).

(4) J. A. Waters, *J. Org. Chem.*, **29**, 428 (1964).

(5) W. A. Bonner and F. D. Mango, *ibid.*, **29**, 430 (1964).

(6) (a) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957); (b) G. J. Karabatsos and C. E. Orzech, Jr., *ibid.*, **84**, 2838 (1962).

(7) P. S. Skell and J. Starer, *ibid.*, **81**, 4117 (1959).

(8) Trademark of E. I. du Pont Co.

(9) M. G. Bloch in H. J. Nobles, R. F. Wall, and N. Brenner, "Gas Chromatography," Academic Press, Inc., New York, N. Y., 1961, pp. 133-161.

butyric acid runs were determined by both methods with good agreement.

Liquid product mixtures obtained by ether extraction of the cell liquid were analyzed by gas chromatography on a 10 ft. silicone gum rubber on Chromosorb column in a F and M Model 500 temperature-programmed gas chromatograph. Calibration was done with known pure compounds. The alcohols and hydrocarbons used for calibration were commercially available materials. The esters were prepared according to conventional methods.

When possible, identification of the products was confirmed by infrared spectroscopy and refractive index measurements on samples isolated by fractional distillation or by preparative gas chromatography on an Autochrome 200 chromatograph.

Electrolyses.—Acetic acid and pentanoic acid electrolyses are summarized in Tables II and III. Butyric acid (250 ml., 2.8 moles) and potassium hydroxide (60 g., 1.0 mole) in water (250 ml.) were electrolyzed at a carbon anode (KC in cell A) for 8 hr. at a current density of 0.047 amp./cm.² at 21 to 26°. From the cell liquid a propyl butyrate fraction was obtained in 12% yield which contained 32% *n*-propyl butyrate and 63% isopropyl butyrate. Pure samples were isolated by preparative scale gas chromatography.

TABLE II
ELECTROLYSIS OF ACETIC ACID

Cell	B	B	A	A
Anode	Pt	Pt	C, (KC)	C, (KC)
CH ₃ COOH, ^a ml.	60	35	360 ^b	250 ^c
(CH ₃ CO) ₂ O, ml.	..	35	...	250
H ₂ O, ml.	4	..	22	...
Current, amp. hr.	4.8	4.8	32	58
C.d., amp./cm. ²	0.11	0.11	0.042	0.042
Applied v. ^d	16-18	36-43	11-15	16-18
T, °C. ^d	26-28	33-37	30-40	39-41

^a Each solution was 0.7 to 0.8 M in anhydrous sodium acetate
^b After 12 amp. hr., 50 ml. added. ^c After 24 amp. hr., 50 ml. added. ^d In most of the electrolyses the applied voltage had to be increased as the reaction proceeded in order to maintain a constant current; consequently, the temperature also increased.

TABLE III
ELECTROLYSIS OF PENTANOIC ACIDS^a

Run	Acid	pH	Anode carbon	Liquid product, g.
432	Pentanoic	6 ^b	KC ^d	10.0
433	Pentanoic	6	KC ^d	10.7
434	Pentanoic	6	TPL	12.8
444	Pentanoic	6	HPL	11.9
448	Pentanoic	8 ^c	KC ^d	6.1
451	2-Methylbutyric	6 ^b	NC60	~9
452	2-Methylbutyric	8 ^c	NC60	1.9
456	3-Methylbutyric	6 ^b	NC60	5.0
487	3-Methylbutyric	6	TPL	14.5
459	3-Methylbutyric	8 ^c	NC60	1.1

^a Cell A, 0.042 ± 0.002 amp./cm.², 18 amp. hr. ^b Acid (70 ml., 0.64 mole), potassium hydroxide (14 g., 0.24 mole), water (400 ml.), 5-25 v., 20-40° (cf. footnote ^d to Table II). ^c Acid (70 ml., 0.64 mole), sodium bicarbonate (90 g., 1.07 moles), water (400 ml.), 5 v., 20-21°. ^d Carbon heated at 900° in CO₂ before use.

Another run was made at a TPL carbon anode with a solution of butyric acid (100 ml., 1.1 moles) and sodium hydroxide (10 g., 0.25 mole) in water (400 ml.) at a current density of 0.034 amp./cm.² and at 20 to 32°. After 2 hr. (8 amp. hr.) sodium sulfate (35 g., 0.25 mole) was added and electrolysis continued. After another 2 hr. the electrolyte was made basic by addition of sodium bicarbonate (80 g., 1.0 mole) and electrolysis continued for 2 hr. A propyl butyrate fraction was obtained in 6% yield which was 26% *n*-propyl butyrate and 69% isopropyl butyrate. Traces of hexane and materials boiling higher than the esters were also found.

Results

Acetic acid was electrolyzed under a variety of conditions to define the most favorable conditions for the

formation of products which might be derived from carbonium ions. The only such product found was methyl acetate. Table IV shows that it was produced only at a carbon anode. In a reaction medium containing water a significantly better yield was obtained than in an anhydrous one. At a platinum anode the only products and their proportions were those expected from a normal Kolbe electrolysis.

TABLE IV
ANODE PRODUCTS FROM ELECTROLYSIS OF ACETIC ACID

Anode	Medium	Methyl acetate, % ^a	Gases, mole %		
			CH ₄	C ₂ H ₄	CO ₂
Pt	H ₂ O	..	0.4	32.6	67.0
Pt	Anhydrous	..	1.0	32.2	66.8
C	H ₂ O	82	2.5	6.4	91.0 ^b
C	Anhydrous	56	4.8	21.4	73.8
			5.5	7.5	87.0 ^b
			8.5	10.0	81.5

^a Current efficiency; yield based on electricity. ^b The first analysis was obtained during the first 25% of reaction and the last during the last 25%.

Anodic oxidation of butyric acid at a carbon anode in aqueous solution produced a gas mixture consisting of 36 ± 1.0 mole % of hydrogen, 17 ± 0.5 propene, 9 ± 0.5 cyclopropane, 35 ± 1.7 carbon dioxide, and 2 ± 1.0 carbon monoxide. This is an average of four gas samples taken during the course of the reaction. The hydrogen, a product of the cathode, may be taken as a measure of the electricity used. Then, the yields of propene and cyclopropane are 47 and 25%. An ester fraction also was obtained in 12% yield, of which 34% was *n*-propyl and 66% was isopropyl butyrate.

An experiment to determine the effect of added salts on the anodic oxidation of butyric acid is shown in Table V. When sodium sulfate and excess sodium bicarbonate were added, the ratio of propene to cyclopropane decreased. The yields of both also decreased. The yields of cyclopropane based on current under the three sets of conditions were 21, 14, and 5%, respectively.

TABLE V
ELECTROLYSIS OF BUTYRIC ACID

Gas	Excess acid	With Na ₂ SO ₄	With NaHCO ₃
H ₂	37.5 ^a	46.4	66.6
Propene	15.5	11.1	4.7
Cyclopropane	8.0	6.6	3.2
CO ₂	37.2	33.6	18.4
CO	..	0.3	2.1
O ₂	0.2	1.6	4.7

^a Mole %, sample taken during last 25% of electrolysis.

From isobutyric acid the products were propene, 60% yield based on current, and isopropyl isobutyrate, 2%.

Electrolyses of the isomeric acids pentanoic, 2-methylbutyric, and 3-methylbutyric at carbon anodes gave methylcyclopropane, all the butene isomers, and nearly all the possible butyl alcohols and butyl pentanoates: Tables VI, VII, and VIII. Gas samples were taken at about eight evenly spaced intervals over the course of the electrolyses. The trends shown in the gas analyses (Tables VI and VII) are corroborated by the untabulated data. Runs 432 and 433 (Table VI) show the reproducibility of electrolyses under identical conditions. The methylbutyric acid electrolyses with

TABLE VI
 HYDROCARBONS FROM PENTANOIC ACID, MOLE %

Run	$n\text{-C}_4\text{H}_{10}$	Butenes				$\text{CH}_3\Delta^b$
		1-	<i>i</i> -	<i>trans</i> -2	<i>cis</i> -2	
432 ^{a,c}	1.3	58.3	3.0	19.2	9.5	8.4
	4.5	49.8	3.8	19.7	12.6	8.6
	3.0	59.3	3.6	17.4	10.8	8.1
433 ^{a,c}	2.0	54.3	4.1	18.3	9.9	10.7
	4.3	48.1	4.1	19.7	13.5	9.6
	2.4	55.9	3.5	19.1	10.7	8.4
434 ^{a,c}	0.6	51.7	3.8	20.4	10.4	12.4
	1.6	49.2	3.6	19.6	12.4	12.9
	2.9	52.5	5.2	17.7	9.8	10.1
444 ^{a,d}	0.6	55.7	1.8	19.2	9.6	12.9
	2.5	52.2	2.1	19.3	12.1	12.4
	3.2	55.5	2.3	17.9	10.8	9.8
448 ^{a,d}	0.5	63.0	...	14.3	7.4	14.8
	2.1	55.1	...	20.0	12.0	10.8
	2.7	54.9	...	18.7	11.9	12.2

^a These mixtures also contained 0.5 to 1.5% cyclopropane, 2 to 5% ethylene, and traces of methane, ethane, C_3H_{10} , C_3H_{12} , and C_6H_{14} . ^b Methylcyclopropane. ^c Plus 3 to 7% propene. ^d Plus 0.5 to 2% propene.

 TABLE VII
 HYDROCARBONS FROM 2-METHYLBUTYRIC (451, 452) AND
 3-METHYLBUTYRIC ACIDS (456, 459, 487), MOLE %

Run	<i>i</i> - C_4H_{10}	Butenes				$\text{CH}_3\Delta$
		1-	<i>i</i> -	<i>trans</i> -2	<i>cis</i> -2	
451 ^{a,b}	0.5	51.5	2.2	27.1	12.7	4.9
	0.7	55.2	2.6	23.6	11.7	4.9
452 ^{a,b}	+	48.8	2.6	29.1	14.5	3.8
	+	45.6	1.8	31.6	16.8	3.5
456 ^{a,c}	5.3	28.8	28.0	18.5	9.9	7.0
	6.2	35.1	22.0	16.1	9.8	6.7
487 ^{a,c}	0.8	30.7	19.5	24.9	11.9	9.3
	1.1	35.5	25.2	16.4	9.5	9.7
459 ^{a,c}	3.7	31.4	26.2	17.0	10.3	8.5
	4.9	31.7	24.4	17.1	9.8	9.8

^a These mixtures also contained 1 to 3% ethylene and traces of methane, ethane, propane, C_3H_{10} , and C_6H_{14} . ^b Plus up to 2% *n*-butane. ^c Plus up to 1% *n*-butane and 2 to 3% propene.

 TABLE VIII
 LIQUID PRODUCTS FROM PENTANOIC ACIDS, %

Run	C_6H_{18}	Butanols			Esters		
		<i>t</i> -	2-	1-	<i>t</i> -	2-	1-
432	6.3	...	15.0	55.9	11.0
433	7.0	...	16.0	50.3	12.0
434	4.7	...	16.1	55.4	10.8
444	6.1	...	15.1	61.4	11.4
448	3.0	...	10.6	1.5	...	64.4	17.3
451	+	+	40.0	+	2.1	39.8	5.4
452	+	...	49.7	+	3.0	37.0	4.5
456	2.4 ^a	4.1	21.7	+	14.5	39.6	+
487	1.8 ^a	5.4	19.5	...	12.9	50.6	...
459	...	2.4	20.0	2.0	8.5	33.7	+

^a 2,5-Dimethylhexane.

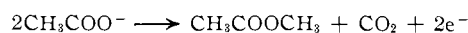
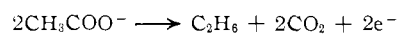
the exception of 487 (Table VII) were made with a more porous carbon anode than were the pentanoic acid electrolyses (Table VI). However, run 487 (Table VII) made with a TPL anode like that used in 434 (Table VI) shows that the greatest difference is in the isobutene content of the product gas which changes in opposite directions in 456 and 487. Hence, no serious error will result from comparing the data for pentanoic acid with that for the methylbutyric acids even though the two sets of data were obtained with different kinds of carbon anodes. In addition to the liquid products

listed in Table VIII there were some unidentified higher boiling ones. No iso esters were found.

The total yields of C_4H_8 compounds obtained from these acids in acidic solutions generally reached a maximum of about 50% in the first half of the electrolysis and decreased to about 35% at its conclusion, while those in slightly basic solutions gradually decreased from 30 to 15%. The total yields of alcohols and esters obtained in acidic electrolyses were about 10% from pentanoic acid and about 20% from the methylbutyric acids. These yields were generally less than half as large in slightly basic solution. All yields are based on current as described earlier.

Discussion

When acetic acid was electrolyzed at a carbon anode the major anodic product was methyl acetate, and the Kolbe electrolysis was greatly suppressed. The composition of the gas from the electrolysis in aqueous solution can be explained if two anodic reactions are occurring simultaneously



If the second reaction occurs at the greater rate the gas composition will approach the earlier analysis, and if the two occur at equal rates the composition will be more like the later analysis (Table IV, third entry).

The formation of methyl acetate in these electrolyses is not unique, but the yields obtained at carbon anodes are significant. For example, a yield of methyl acetate of only 2% has been reported in the electrolysis of acetic acid at a platinum anode.¹ None was found in the present work. The conversion of acetic acid to methanol by electrolysis is also known¹—the Hofer-Moest reaction. It is promoted in neutral or alkaline solution in the presence of inert anions such as sulfate, phosphate, perchlorate, carbonate, and bicarbonate. Carbon anodes have some advantage over platinum in the Hofer-Moest reaction, but the value of carbon anodes in the production of these oxygenated products, especially esters, by electrolyses which normally yield hydrocarbons has not generally been appreciated. Another similar reaction which is promoted at carbon anodes is the formation of ethers by electrolysis of acids in alcoholic solutions containing inert salts.



No ethers are obtained at a platinum anode, and the absence of inert salts reduces the ether yield to about one-third.¹⁰

In view of the superior yield of methyl acetate at a carbon anode in aqueous solution, these conditions were used in all subsequent anodic oxidations from which products which might arise from carbonium ion intermediates were sought.

Anodic oxidation of butyric acid at a carbon anode in the presence of an excess of the acid produced an 84% total yield based on current of abnormal products: propene, cyclopropane, and propyl butyrates. The cyclopropane to propene ratio (1:2) obtained from butyric acid may be compared with that (1:9) obtained by deamination of *n*-propylamine or deoxidation of *n*-propyl alcohol,¹¹ and the *n*- to isopropyl butyrate

TABLE IX
 COMPARISON OF BUTYLCARBONIUM ION FORMING REACTIONS, ELIMINATION PRODUCTS

Reaction	Butenes			C ₃ H ₆ , mole %	Ref.
	2-/1-	<i>trans/cis</i>	<i>t</i> , mole %		
Electrolysis of pentanoic acid	0.5-0.7	1.5-2.0	3-4	8-13	
Deamination of butylamine	0.41 ^a	2.2	0		6a
	0.67 ^b	1.7			15
Deoxygenation of 1-butanol		1.85		2	7, 11
Electrolysis of 2-methylbutyric acid	0.6-0.8	1.9-2.2	~2	3-5	
Deamination of <i>sec</i> -butylamine	3.0 ^a	2.9			6a
	3.55 ^b	2.1			15
Deoxygenation of 2-butanol		1.67		<0.5	7, 11
	1.37	1.66	...	Trace	c
Electrolysis of 3-methylbutyric acid	0.7-1.2	1.6-2.1	20-30	7-10	
Deamination of isobutylamine	2.67	1.40	34		16
Deoxygenation of isobutyl alcohol		1.82	Some	4	11
	0.77	1.60	55	5	c

^a In acetic acid at room temperature. ^b In water at 70°. ^c Procedure of Skell and Starer¹¹ was used.

ratio (30:70) with the corresponding alcohol ratio (30:70) obtained by deamination of 1,1,2,2-*d*₄-1-amino-propane.^{6b} The formation of cyclopropanes has been reported to be a fundamental reaction of carbonium ions.¹² These products indicate carbonium ion intermediates in the anodic oxidation of butyric acid. The greater cyclopropane to propene ratio suggests that the electrochemically generated carbonium ions are more reactive than those arising from deamination or deoxidation.

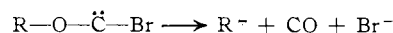
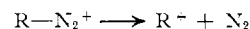
The experiment of Table V shows that the best yield of propene and cyclopropane is obtained when the anodic oxidation is conducted in an excess of butyric acid with no added salts. This result appears contrary to predictions based on the Hofer-Moest reaction in which added salts favor the formation of abnormal or carbonium ion products. However, the Hofer-Moest reaction is generally carried out with a platinum anode. Then added salts favor carbonium ion products relative to the normal radical products. At a carbon anode even without the help of added salts or increased pH, radical product formation is practically completely eliminated. Then the salts only promote oxygen evolution and further oxidation of organic compounds at the anode. The change in the propene to cyclopropane ratio may be attributed not to a change in their rates of formation but to preferential consumption of propene in further reactions at the anode.

The superiority of a carbon anode for generation of carbonium ions is also evident with the pentanoic acids. The octanes in Table VIII and the butanes in Tables VI and VII show the small extent to which the Kolbe electrolysis competes with the carbonium ion forming oxidation at carbon anodes. In the Kolbe electrolysis at platinum electrodes¹³ pentanoic acid yields 50% of Kolbe dimer, octane, 18% of olefin, and 4% of ester; 3-methylbutyric acids yields 43% of 2,5-dimethylhexane, 42% of olefin, and 5% of ester; and 2-methylbutyric acid yields 10% of an octane, 42% of olefin, and 10% of ester.

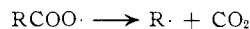
The products of the electrolyses of the pentanoic acids at carbon anodes¹⁴ and of deamination of butyl-

amines¹⁵⁻¹⁷ and deoxidation of butyl alcohols^{7,11} (Table IX) indicate that similar intermediates determine the products in all of these reactions. In the latter two cases these intermediates are accepted as being carbonium ions.^{6a,12,15,16} Carbonium ions¹⁸ most readily explain the electrolysis products also. However, the electrolysis products cannot completely rule out all other kinds of intermediates. For example, butyl radicals generated at a carbon anode might yield the observed products as a result of some specific association with or stabilization by the anode. Since there is no evidence that the product-determining intermediates are butyl radicals, and since the products are not those expected from radicals in conventional reactions, the electrolysis will be discussed in terms of carbonium ions.

Pentanoic acid, *n*-butylamine, and 1-butanol yield very similar proportions of butene isomers (Table IX). The reactions of all three can be explained by *n*-butylcarbonium ions. The greater proportions of methylcyclopropane and isobutene found in the electrolysis products suggests that less selective, *i.e.*, higher energy, carbonium ions are generated at carbon anodes rather than in solution. In deamination^{6a} and deoxidation¹² the carbonium ion intermediates result from the loss of neutral molecules from cationic or neutral precursors



In the anodic reaction also neutral molecules must be lost, but they are thought to be lost before the cationic species are generated



However, it is conceivable that at a carbon anode the carboxylate radicals are stabilized sufficiently to be oxidized further to cationic species, RCOO⁺, which could be decarboxylated directly to carbonium ions. Then parallel mechanisms could explain the products (at least the unbranched butenes) of all three reactions. The analogy is weakened somewhat by the isomer dis-

(11) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **82**, 2971 (1960).

(12) P. S. Skell and I. Starer, *ibid.*, **84**, 3962 (1962).

(13) C. J. Brockman, "Electro-Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1926.

(14) The C₄H₈ isomer data (Table IX) from the electrolyses are presented as ranges because they change with the electrolysis time and these changes are not understood.

(15) W. B. Smith and W. H. Watson, Jr., *J. Am. Chem. Soc.*, **84**, 3174 (1962).

(16) L. G. Cannell and R. W. Taft, Jr., *ibid.*, **78**, 5812 (1956).

(17) F. C. Whitmore and D. P. Langlois, *ibid.*, **54**, 3441 (1932).

(18) When the term "carbonium ion" is used in this discussion no implications regarding its structure or environment are intended.

tribution in the substitution products. Electrolysis yields *n*- and *sec*-butyl esters¹⁹ in a 17:83 ratio, while deamination yields a 65:35 ratio.^{6a,17} Streitwieser and Schaeffer^{6a} have explained the deamination data on the basis of a concerted loss of nitrogen from the diazonium ion and a hydride shift to the primary carbon. The electrolysis data, on the other hand, are not consistent with such a concerted mechanism. The *n*- to *sec*-butyl ester ratios and the 2- to 1-butene ratios obtained by electrolysis are consistent with each other if the esters and the butenes are formed from the same mixture of *n*- and *sec*-butylcarbonium ions, and if butenes are formed from the *sec*-butylcarbonium ions by random loss of 1- or 3-protons.

In the reactions of 2-methylbutyric acid, *sec*-butylamine, and 2-butanol, *sec*-butylcarbonium ions can be intermediates. The *trans* to *cis* ratios (Table IX) are reasonably close for the three reactions, but the 2- to 1-butene ratios are very different. In the electrolysis there is a marked preference for 1-butene formation. The 2- to 1-butene ratio again suggests random elimination of 1- and 3-protons from *sec*-butylcarbonium ions. Among the substitution products from the electrolysis (Table VIII) is some *n*-butyl ester. This suggests rearrangement of secondary to primary carbonium ions. No such rearrangement has been reported in the deamination of secondary amines. Furthermore, 2-butene is the predominant elimination product from *sec*-butylamine. The deamination is believed to involve a concerted loss of nitrogen molecules and protons. Although all three reactions can be explained by carbonium ions, the details of the explanations must be quite different.

From 3-methylbutyric acid, isobutylamine, and isobutyl alcohol, isobutylcarbonium ions might be generated. Again the *trans* to *cis* ratios are reasonably close, while there is a greater variation among the 2- to 1-butene ratios. The extent of methyl migration in the isobutylcarbonium ions is only slightly greater in the electrolysis than in deamination, but the rearranged species from the latter has a much greater preference for 2-butene formation than that from the former. Very similar unbranched butene isomer distributions are obtained by electrolysis and deoxidation. The proportions of methylcyclopropane are not greatly different. However, methyl migration occurs to a substantially greater extent in electrolysis than in deoxidation. Marked differences also appear in the substitution products. From electrolysis of 3-methylbutyric acid the major substitution product is the *sec*-butyl ester (*sec*:*t* = 76:24) while from deamination it is the *t*-butyl isomer (*sec*:*t* = 10:71).

Comparing the electrolysis products from the three acids (Table IX) shows a marked similarity in the 2- to 1-butene and *trans*- to *cis*-2-butene ratios. These butenes seem to be formed from the same intermediates regardless of the acid used. The 2- to 1-butene ratio

(19) The isomer distribution in the liquid electrolysis products is based on the esters because of the susceptibility of the alcohols to oxidation.

(allowing for that 1-butene which is formed from *n*-butylcarbonium ions) is close to that expected (0.67) from *sec*-butylcarbonium ions through random elimination of either 1- or 3-protons. Such a nonselective elimination reaction requires a fairly energetic intermediate. Such an intermediate ought to be structurally similar to the free carbonium ion envisioned as the intermediate in a true E1 elimination.¹⁵ Then there should be no preference for *trans*- or *cis*-2-butene formation in the elimination reaction. The observed *trans* to *cis* ratios (Table IX) rule out a free carbonium ion of the E1 type.

The product data from the electrolyses do not allow a clear description of the anodic oxidation mechanism, but the following description is not unreasonable. At the anode an alkyl radical is generated *via* the usual Kolbe sequence and then oxidized to a carbonium ion. This carbonium ion is a higher energy species, a "hot" carbonium ion,²⁰ than those involved in conventional carbonium ion reactions. This "hot" intermediate yields products by way of two paths: (1) It undergoes elimination reactions which yield the cyclopropanes and a part of the olefins. (2) It undergoes rearrangements (either hydride or methyl migrations) to more stable intermediates. Then these second stage intermediates yield olefins and substitution products. At this stage some specific association of the carbonium ion intermediate with the anode seems necessary to explain the 2- to 1-butene and *trans*- to *cis*-2-butene ratios obtained from the isomeric pentanoic acids. This idea cannot be tested nor can further speculation be justified until a kinetic study of the electron-transfer processes has been made.

A better analogy for the reactions of the electrochemically generated butylcarbonium ions might be found in the oxidation of butyl radicals by copper(II) salts. *sec*-Butyl radicals are oxidized by simple cupric salts to butenes which have a 2-:1- ratio of about 0.85 and a *trans*:*cis*- ratio of 0.92 to 1.5 (at 30 to 40°).²¹ Complex cupric salts yield ratios of 0.87 and 1.9, respectively. Kochi²¹ has proposed a simultaneous electron transfer and β -hydrogen elimination to explain the former result and an electron transfer to form a relatively free carbonium ion in the latter case. The butene ratios obtained from the relatively free carbonium ion are very close to those obtained by electrolysis of 2-methylbutyric acid (Table IX). The carbonium ions are formed by an electron transfer in both cases. However, this analogy fails completely when *n*- and isobutylcarbonium ions are considered. Cupric salts converted *n*- and isobutyl radicals exclusively to 1-butene and isobutene, respectively.

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(20) M. S. Silver, *J. Org. Chem.*, **28**, 1686 (1963).

(21) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963).