(IV) with *cis*- and *trans*-1,2-cyclopentanediols is less certain since these reactions could not be studied under conditions permitting determination of the equilibrium constant for complex formation. However, the entropies of activation for these compounds suggested that the *trans*-diol is oxidized *via* an acyclic mechanism.

Substitution of a methyl group for a hydroxyl hydrogen apparently prevents chelate complex formation with cerium(IV). However, *trans*-1,2-cyclohexanediol and *trans*-2-methoxycyclohexanol are oxidized by cerium(IV) at approximately the same rate, although the complex formed with these compounds is different. Thus, the nature of the complexes formed in cerium(IV) oxidations cannot be determined from measurements of relative rates of oxidation.

For reaction media containing from 0.25 to 0.75 *M* sulfuric acid, the cerium(IV)–sulfate complexes $CeSO_4^{2+}$, $Ce(SO_4)_2$, and $Ce(SO_4)_3^{2-}$ participate in the oxidation reaction. The reactivities of the various species increase as the number of sulfate ions in the complex decreases, and in the range of sulfate ion concentrations studied the $CeSO_4^{2+}$ species accounts for a major portion of the reaction.

The relative reactivities of certain cellulose model compounds suggest that in the cerium(IV)-initiated graft polymerization onto cellulose, the oxidation reaction of cerium(IV) with cellulose will occur mainly at the C_2–C_3 glycol unit and to a lesser extent at the C_6 primary hydroxyl.

Registry No.—Cyclohexanol, 108-93-0; cyclopentanol, 96-41-3; *cis*-1,2-cyclohexanediol, 1792-81-0; *trans* isomer of **5**, 1460-57-7; *trans*-2-methoxycyclohexanol, 7429-40-5; *cis* isomer of **8**, 7429-41-6; *trans*-1,2-cyclopentanediol, 5057-99-8; *trans*-2-methoxycyclopentanol, 7429-45-0; *cis*-1,2-cyclopentanediol, 5057-98-7; cyclohexanemethanol, 100-49-2; tetrahydropyran-2-methanol, 100-72-1; glutaraldehyde bis(*cis*-1,2-cyclopentanediol acetal, 7616-85-3.

Acknowledgments.—The authors appreciate the comments and suggestions of Drs. J. W. Green and D. G. Williams.

Electrolyses of Mixtures of Carboxylic Acids

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Received May 9, 1966

Formic acid, acetic acid, propionic acid, and trifluoroacetic acid have been electrolyzed competitively in mixtures of pairs. In terms of the products formed in these competitive electrolyses, formic and trifluoroacetic acids are comparable in ease of electrolysis, both are more readily electrolyzed than acetic and propionic acids, and these last two are comparable with each other. These results are not entirely consistent with the conclusions that would be drawn from voltammetric data in the literature, and the deviations are rationalized on the basis of differences in ionization among the acids.

During a continuing study of anodic reactions of carboxylic acids, it became desirable to obtain knowledge of the relative electrochemical behavior of several acids.

In previous work, formic and acetic acids were electrolyzed in the presence of various added substrates, notably hydrocarbons[1] and amides.[2,3] Rates of gas production were measured and both gaseous and liquid products were determined.

In the present study, a number of competitive electrolyses were conducted on mixtures of acids under conditions similar to those previously employed, again measuring rates of gas production and analyzing the gaseous products. The information thus obtained permits a determination of the relative ease of anodic discharge of the various acids. The acids used were formic, acetic, propionic, and trifluoroacetic.

Experimental Section

Apparatus and Gas Analyses.—The electrolysis cell has been described previously.[1] Electrolyses were conducted at 0.40 or 0.20 amp provided by a constant-current power supply. The cell was connected to a gas-measuring apparatus, also described previously,[4] with which the rate of gas production was measured. Samples of the gas were analyzed with a Perkin-Elmer Model 154 vapor fractometer, using a Perkin-Elmer J column (silica gel packing) and a gas-sampling valve for reproducing sample sizes.

Materials.—The glacial acetic acid used was ACS grade from the General Chemical Division of Allied Chemical Co. Formic acid, from the same source, was CP grade 98–100%. Analyzed, reagent grade potassium acetate was obtained from the J. T. Baker Chemical Co. Sodium formate was Fisher Scientific Co. purified grade. Fisher certified reagent grade propionic acid was redistilled and a cut boiling at 49° (14 mm) was used. Trifluoroacetic acid was redistilled and a middle cut boiling at 69° was used. Sodium trifluoroacetate was prepared by neutralization of trifluoroacetic acid. Gases used as standards for vpc analyses were obtained from the Matheson Co. and were of the highest purity available in lecture bottles.

Results

Mixed Formic and Acetic Acids.—When a solution of potassium acetate (5.0 g) in glacial acetic acid (60 ml) is electrolyzed at 20° at 0.40 amp (1 cm² platinum electrodes at a separation of 0.6 cm) the rate of total gas production is 100 ± 1% of that demanded by eq 1 and 2 and the gas contains the proper amounts of carbon dioxide and ethane.[1]

$$2H^+ + 2e \longrightarrow H_2 \quad (1)$$

$$2CH_3COO^- \longrightarrow 2CO_2 + C_2H_6 + 2e \quad (2)$$

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[1] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **86**, 4139 (1964).

[2] S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **86**, 2745 (1964).

[3] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **31**, 128 (1966).

[4] R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

When a solution containing potassium formate in 98+% formic acid is electrolyzed under the same conditions, the rate of gas production is 99.1–99.6% of that required by eq 1 and 3 and the gas contains the proper proportion of CO_2.[1,3] Conway and Dziechiuch

$$HCOO^- \longrightarrow CO_2 + H^+ + 2e \quad (3)$$

have also confirmed that eq 1 and 3 represent the cathodic and anodic reactions, respectively, for the electrolysis of formic acid.[5]

Equations 1–3 show that for a given electrolysis current the rate of gas production in the acetate case is twice the rate in the formate case. Also, the gas in the acetate case is composed of 25% H_2, 25% ethane, and 50% CO_2 (on a molar basis), while the formate gas is 50% H_2 and 50% CO_2. In volume per cent, based on ideal mixing of the real gases, the acetic acid gas should be 25.17% H_2, 24.87% ethane, and 49.96% CO_2, while the formate gas should be 50.19% H_2 and 49.81% CO_2.

We have now electrolyzed mixtures of formic and acetic acids in approximate molar ratios of 2:1, 1:1, and 1:2 at 0.40 amp in the same apparatus as was previously used for the individual acids.

With an initial formic–acetic ratio of 2:1 (34.0 ml, 0.906 mole of HCOOH; 3.4 g, 0.050 mole of sodium formate; 27.0 ml, 0.472 mole of CH_3COOH), the electrolysis was run for 51 hr during which time the gassing rate was almost constant, varying only from 103.0 to 103.8% of theoretical formate gas (eq 1 and 3). The gas compositions for two points, at 3 and 27 hr after the start of the electrolysis, are shown in Table I.

TABLE I

Time, hr	% (by volume) CO_2	C_2H_6	CH_4	H_2	Total
3	49.4	0.5	0.1	48.7	98.7
27	50.3	0.7	0.2	48.4	99.6

Since hydrogen cannot be readily determined by gas chromatography, the reported H_2 percentages are not true analyses, but have been calculated from charge passed and volume of gas collected, assuming the validity of eq 1. The deviations from 100% of the sums of all the percentages include any inadequacy of this assumption and also include errors in the vpc analyses as well as failure to detect any component of the gas mixture.

In the equimolar mixture (38.0 ml, 0.664 mole of CH_3COOH; 23.0 ml, 0.613 mole of HCOOH; 3.7 g, 0.054 mole of sodium formate), electrolyzed at 0.40 amp, the gassing rate begins at about 105% of the theoretical formate gassing rate and increases slowly with time, reaching 108.8% after 36 hr and 115.2% after 59.5 hr. The gas compositions are shown in Table II.

TABLE II

Time, hr	% (by volume) CO_2	C_2H_6	CH_4	H_2	Total
36	50.4	2.6	0.2	46.2	99.4
59.5	50.8	5.4	0.4	43.6	100.2

In the 1:2 formic–acetic mixture (45.0 ml, 0.786 mole of CH_3COOH; 13.0 ml, 0.346 mole of HCOOH; 3.4 g, 0.050 mole of sodium formate), electrolyzed at 0.40 amp, the gassing rate after 1.8 hr was 108.8% of theoretical formate gassing and it had risen to 110.2% after 3.7 hr of electrolysis. The gas compositions are given in Table III.

TABLE III

Time, hr	% (by volume) CO_2	C_2H_4	CH_4	H_2	Total
1.8	50.5	3.5	0.3	46.1	100.4
3.7	51.0	3.6	0.3	45.5	100.4

In all of these mixtures it is apparent that most of the current is used for the electrolysis of formic acid, with acetic acid electrolysis increasing slightly with increased initial total acetate concentration, and also increasing slowly with time in any one mixture (as HCOOH is depleted), this time dependence being most noticeable when the initial HCOOH concentration is smallest. The increase in gassing rate is in every case paralleled by an increase in ethane concentration in the gas mixture.

Trifluoroacetic Acid Electrolysis.—A solution of 6.8 g (0.050 mole) of sodium trifluoroacetate in 56.0 ml (0.754 mole) of trifluoroacetic acid was electrolyzed at 0.40 amp in the same cell as was used for the formic and acetic acid electrolyses. If the reaction of CF_3COOH proceeds analogously to that of CH_3COOH, eq 1 and 4 apply. The rate of gas production demanded

$$2CF_3COO^- \longrightarrow 2CO_2 + C_2F_6 + 2e \quad (4)$$

by eq 1 and 4 is 102.3% (by volume) of that required by eq 1 and 2 for CH_3COOH and 204.0% of that required by eq 1 and 3 for HCOOH. The gaseous product will be 24.61% H_2, 26.55% hexafluoroethane, and 48.85% CO_2.

Measurements of the gassing rate at 0.9 and 2.4 hr after the start of the electrolysis showed 95.4 and 97.5%, respectively, of that required by eq 1 and 4. The compositions are shown in Table IV. Thus it appears that the electrolysis of trifluoroacetic acid obeys eq 1 and 4 at least reasonably well.

TABLE IV

Time, hr	% (by volume) CO_2	C_2F_6	CF_4	CO	H_2	Total
0.9	47.1	26.3	0.4	0.2	25.8	99.8
2.4	49.7	23.0	1.0	0.3	25.2	99.2

Mixed Acetic and Trifluoroacetic Acids.—A solution of 4.91 g (0.050 mole) of potassium acetate in 24.0 ml of acetic acid (0.419 mole) and 35.0 ml (0.471 mole) of trifluoroacetic acid was electrolyzed at 0.40 amp. This solution is approximately equimolar in total acetate and trifluoroacetate. Measurements of gassing rate at 2.0 and 4.2 hr after the start of electrolysis show 98.7 and 99.2%, respectively, of theoretical acetate gassing (96.5 and 97.0% of theoretical trifluoroacetate gassing). The compositions of these two gas samples are given in Table V.

TABLE V

Time, hr	% (by volume) CO_2	C_2F_6	CO	H_2	Total
2.0	46.3	25.2	0.1	25.5	97.1
4.2	46.3	24.8	0.1	25.4	96.6

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[5] B. E. Conway and M. Dziechiuch, *Can. J. Chem.*, **41**, 21 (1963).

No trace of either ethane or CF_4 could be detected. It thus appears that trifluoroacetic acid is electrolyzed to the virtual exclusion of acetic acid.

Mixed Formic and Trifluoroacetic Acids.—A solution of 3.0 g (0.044 mole) of sodium formate in 18.0 ml (0.477 mole) of formic acid and 40.0 ml (0.521 mole) of trifluoroacetic acid was electrolyzed at 0.40 amp. The rate of gassing was found to be about midway between formic and trifluoroacetic theoretical gassing rates, with one measurement at 1.1 hr after the start of electrolysis showing 155.5% of the theoretical formate rate and a second point at 4.4 hr showing 143.0%. The gas compositions are given in Table VI. Formic acid is known, under some conditions, to decompose to water and carbon monoxide in the presence of strong acids.[6,7] This possible source of carbon monoxide was investigated by placing a duplicate of the electrolysis solution in the electrolysis cell connected to the gas collection apparatus and determining that no gas was generated. The solution was next electrolyzed briefly, the source of power was then disconnected, and again no gas was generated in the absence of electrolysis. It must be concluded that the carbon monoxide is a product of electrochemical reaction.

TABLE VI

Time, hr	% (by volume)					
	CO_2	C_2F_6	CF_4	CO	H_2	Total
1.1	47.0	15.9	0.5	6.1	33.0	102.5
4.4	48.5	9.3	0.8	7.8	35.1	101.5

In spite of the uncertainty about the origin of the carbon monoxide, the gassing rates and the quantities of fluorinated products indicate that formic and trifluoroacetic acids compete about equally well in the discharge reaction.

Two other mixtures of formic and trifluoroacetic acids were electrolyzed without analyzing the gaseous products. Their ratios of total formate/total trifluoroacetate were 3.7:1 and 1:3.4. In the first of these, a solution of 2.0 g (0.029 mole) of sodium formate in 35.0 ml (0.927 mole) of formic acid and 20.0 ml (0.260 mole) of trifluoroacetic acid was electrolyzed at 0.40 amp. The rate of gas formation was found to be 129.5% of the theoretical formate rate after 2.1 hr of electrolysis and decreased to 118.8% after 4.8 hr. In the other, a solution of 2.0 g (0.029 mole) of sodium formate in 6.0 ml (0.159 mole) of formic acid and 49.0 ml (0.638 mole) of trifluoroacetic acid was electrolyzed at 0.40 amp. In this case the rate of gas production after 1.2 hr of electrolysis was 180.0% of that predicted by eq 1 and 3 for formic acid and it decreased to 167.6% after 2.2 hr and 146.9% after 4.4 hr.

The product variation with time in these mixtures cannot be explained by depletion of one of the components, but must result from a perturbation of the anode reaction by products of the electrolysis.

Mixed Acetic and Propionic Acids.—A solution of 5.0 g (0.051 mole) of potassium acetate in 26.0 ml (0.454 mole) of acetic acid and 34.0 ml (0.455 mole) of propionic acid was electrolyzed at 0.20 amp. The solution was not sufficiently conducting to permit convenient electrolysis at 0.40 amp, and solutions of propionate salts in propionic acid alone could not be electrolyzed at any reasonable current. Many measurements were made of gassing rates, with nearly all of them falling in the range 95 to 99% of theoretical acetic acid Kolbe gassing rate (eq 1 and 2). The analogous equations for the Kolbe electrolysis of propionic acid are eq 1 and 5. The coupling product, *n*-butane, is ordinarily

$$2CH_3CH_2COO^- \longrightarrow 2CO_2 + C_4H_{10} + 2e \qquad (5)$$

not obtained in good yield from the electrolysis of propionic acid, and ethylene is a much more common product.[8]

In the mixture of acetic and propionic acids, analysis of the gas collected at 7.3 hr after the start of the electrolysis, at 99.1% of theoretical acetate gassing rate, gave the following data (% by volume): CO_2, 49.5; CH_4, 1.7; C_2H_6, 9.6; C_2H_4, 4.1; C_3H_8, 8.8; H_2, 25.4; and total, 99.1. No butane was detected.

Assuming that all methane and ethane come from acetic acid, all ethylene comes from propionic acid, and propane results from discharge of one of each (coupling of a methyl radical from acetate and an ethyl radical from propionate), this gas analysis indicates that nearly identical quantities of each of the two acids are reacting.

Discussion

We have observed that acetic and propionic acids compete about equally in anodic oxidation. Pande and Shukla have shown that propionate, butyrate, valerate, and caproate have very similar current–potential curves in solutions 1 *N* in the acids and in their sodium salts.[9] Eberson[10] has computed that the standard electrode potentials for removal of an electron from acetate and propionate are fairly close to each other, with the potential for propionate being 0.18 volt less than that for acetate. Acetic and propionic acids are also quite similar in acid strength, with acetic acid being slightly stronger. In view of these facts, our observation might well have been predicted.

Pande and Shukla[9] also showed that the current–potential curve for formate falls about 0.35 v below that for propionate, and, if acetate and propionate can be assumed to be comparable in discharge characteristics, then formate would be expected to react at the anode in preference to acetate. This is what we observe. Formic acid is also a stronger acid than acetic by an order of magnitude, and formate ions would be expected to predominate over acetate ions in our mixtures of these two acids. This factor might also be expected to favor formate electrolysis in preference to acetate.

Voltammetric measurements by Conway and Dzieciuch indicate that the current–potential curve for formic acid falls at an anode potential 0.6–2.0 v lower than the curve for trifluoroacetic acid.[11] On this basis, formate electrolysis would be expected to predominate in a mixture of formic and trifluoroacetic acids. Instead, we find that, in an equimolar mixture, the two acids compete about equally well, and that when

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[6] E. R. Schierz and H. T. Ward, *J. Am. Chem. Soc.*, **50**, 3240 (1928).

[7] A. I. Gel'bshtein, G. G. Shcheglova, and M. I. Temkim, *Zh. Fiz. Khim.*, **30**, 2267 (1956); *Chem. Abstr.*, **51**, 9271*i* (1957).

[8] M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958, p 103.

[9] G. S. Pande and S. N. Shukla, *Electrochim. Acta*, **4**, 215 (1961).

[10] L. Eberson, *Acta Chem. Scand.*, **17**, 2004 (1963).

[11] B. E. Conway and M. Dzieciuch, *Can. J. Chem.*, **41**, 38 (1963).

formic acid is present in excess the rate of gas production is closer to that expected for formic acid alone, while excess trifluoroacetic acid leads to a rate of gas formation closer to that observed for trifluoroacetic acid alone. The observations can be rationalized by noting that trifluoroacetic acid is a much stronger acid than formic acid, resulting in a predominance of trifluoroacetate ions over formate ions, and that this predominance of trifluoroacetate ions could be sufficient to overcome the apparent difference in potentials for the two reactions.

The previously cited comparisons of discharge potentials[9-11] would place acetate discharge at a considerably lower potential than trifluoroacetate discharge. We have found, however, that trifluoroacetic acid is anodically oxidized to the virtual exclusion of acetic acid. This again can be explained by the much greater ionization of trifluoroacetic acid and it is entirely consistent with our observations in the formic acid–acetic acid and formic acid–trifluoroacetic acid mixtures.[12]

Registry No.—Formic acid, 64-18-6; acetic acid, 64-19-7; trifluoroacetic acid, 76-05-1; propionic acid, 79-09-4.

[12] A referee has suggested that voltammetric measurements (details not specified) should be reported for these systems. We have cited results of such measurements from the literature and have pointed out that conclusions based on these data do not explain our observations. The primary difficulty resides in the indeterminacy of liquid–liquid junction potentials (see Ives and Janz, "Reference Electrodes," Academic Press Inc., New York, N. Y., 1961, pp 50, 439). Measurements made in one acid simply cannot be related to data from another acid solvent. We might make measurements in solutions containing low concentrations of our acid anions in the presence of a high concentration of an indifferent electrolyte, thereby relating the anions to one another, but these data could not be translated to the systems that we have studied. Our work must be construed as a distinctly separate approach to which voltammetric data can be related crudely at best.

Ring-D-Bridged Steroid Analogs. III.[1] Hunsdiecker Reaction of *endo*-Norborn-5-ene-2-carboxylic Acids[2]

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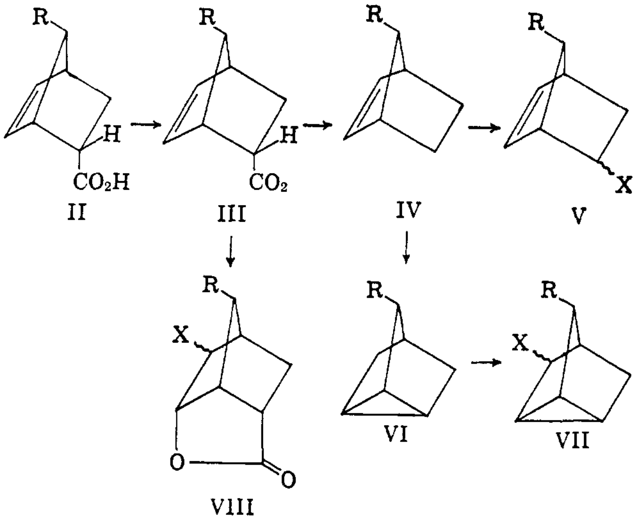
Received May 3, 1966

14α,17α-Etheno-16α-carboxypregn-5-en-3β-ol-20-one acetate was found to undergo the Cristol modification of the Hunsdiecker reaction to afford a *cis*-iodo lactone. In contrast, under the same conditions, *endo*-norborn-5-ene-2-carboxylic acid formed a *trans*-iodo lactone. The differing steric nature of the products is attributed to steric hindrance, on the backside of the double bond, in the steroid.

We have been attempting to synthesize 14α,17α-etheno- (or ethano-) pregn-4-ene-3,20-dione in order to determine the effect of such a 14α,17α-hydrocarbon bridge on the biological activity of progesterone. We have therefore been investigating various possible approaches to the removal of the carboxylic acid moiety from 14α,17α-etheno-16α-carboxypregn-5-en-3β-ol-20-one (Ia). Lack of success, in attempts[4] to reduce selectively the ring-D double bond of the adducts[5] resulting from Diels–Alder addition of maleic anhydride or of 4-phenyl-1,2,4-triazoline-3,5-dione to 3β-acetoxy-17-cyano-5,14,16-androstatriene, discouraged us from attempting to reduce selectively the corresponding double bond of I. Therefore, we decided to subject compound Ib to the conditions of the Cristol–Firth[6] modification of the Hunsdiecker reaction.[7]

A free-radical mechanism has been suggested for the Hunsdiecker reaction and apparently also pertains to the Cristol–Firth modification.[8] This mechanism leads to the prediction that the reaction of an *endo*-norborn-5-ene-2-carboxylic acid (II) should proceed by way of carboxy radical III. Decarboxylation of III should lead to alkyl radical IV which can either halogenate to give the normal Hunsdiecker product V[9] or yield, *via* the rearranged radical VI, the nortricyclyl halide VII.[10] Alternatively, the carboxy radical III could add to the double bond to afford halo lactone VIII. A concerted attack on the double bond should lead to *trans* addition, giving a product identical with that expected to be derived from a Prevost reaction[7] of the starting material. Nonconcerted addition



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[2] This work was supported in part by Grants AM-06900-03 and AM-06900-04 from the National Institutes of Arthritis and Metabolic Diseases, The National Institutes of Health, U. S. Public Health Service.

[3] To whom inquiries regarding this work should be addressed.

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