Electrolysis of α-bromocarboxylic acids

R. G. WOOLFORD, JUDY SOONG, AND W. S. LIN
Department of Chemistry, University of Waterloo, Waterloo, Ontario

Received September 1, 1966

The electrolysis of α-bromovaleric, α-bromocaproic, α-bromodiethylacetic, and α-bromoisobutyric acids in both methanol and water has been studied. This represents the first detailed study of the behavior of α-halocarboxylic acids during Kolbe electrolysis.

Under the experimental conditions, Kolbe dimer of the α-bromoacid is not produced, even in small amounts, in either solvent. In methanol, hydrogen ester and bromoester were the major electrolysis products. In water, straight-chain acids gave alkyl halide, 1,1-dibromoalkane, and Kolbe dimer of hydrogen acid, whereas branched-chain acids gave ketone and other products from bromination of the ketone. In both solvents, considerable free bromine was produced.

Canadian Journal of Chemistry. Volume **45**, 1837 (1967)

The Kolbe electrolysis of an acid RCOOH to yield dimer R—R usually occurs smoothly at a platinum anode when R is an alkyl group with no substituent at the α-carbon. The mechanism is generally regarded as a free radical process where $RCOO^-$ is oxidized to $RCOO\cdot$, which decarboxylates to $R\cdot$. Dimer R—R forms by combination of two $R\cdot$ radicals, and by-products such as esters, ethers, and hydrocarbons can be explained by reactions of $RCOO\cdot$ and $R\cdot$ with the solvent or with themselves. However, when α-substituents are present, dimerization does not always occur and other products are obtained which are often typical of carbonium ion processes (for more details, see ref. 1 and articles cited therein).

Most α-alkyl-substituted acids and cycloalkyl acids give small or negligible yields of dimer on electrolysis (e.g. 2–4), apparently because the secondary or tertiary radical produced at the anode is further oxidized to a carbonium ion which often reacts with the solvent. Calculations (5) indicate that carbonium ions should be formed predominantly where $R\cdot$ has an ionization potential lower than about 8 eV (most secondary, tertiary, alicyclic, and benzylic radicals are in the range 7–8 eV, whereas primary radicals are higher). Fair yields of dimer are obtained from some α-substituted acids, where the radicals produced have, or can be assumed to have, high ionization potentials due to stabilization by delocalization of the unpaired electron over an unsaturated group such as COOEt (6, 7), CN (8), and $CONH_2$ (9). No coupling reactions have been reported for any α-halogenocarboxylic acids, except for trifluoroacetic acid (10, 11), and in fact there have been few attempts to study their electrolysis reactions.

Troeger and Ewars (12) first described the electrolysis of chloroacetic acid in water, and Kaufler and Herzog (13) conducted a systematic analysis of the products. The two major products were methylene chloride and chloromethyl chloroacetate, and the gases evolved were Cl_2, CO, CO_2, and HCl. Methylene chloride was a surprising product, but no ethylene chloride (i.e. Kolbe dimer) was obtained. A mechanism was proposed involving radicals $ClCH_2COO\cdot$ and $ClCH_2\cdot$ as well as $Cl\cdot$ from decomposition of $ClCH_2COO\cdot$ into $Cl\cdot$, CH_2O, and CO. Except for limited amounts of unidentified esters, similar products were obtained from bromoacetic, iodoacetic, dichloroacetic, and trichloroacetic (14) acids. Difluorochloroacetic acid gave CF_2Cl_2 as major product (10).

Thiessen and Miller (15) electrolyzed potassium α-bromopropionate in concentrated aqueous solution and obtained ethylidene bromide, CH_3CHBr_2, in very poor yield (not calculated, but apparently less than 10%), free bromine, and unidentified other products. The additional Br gained by $CH_3CHBr\cdot$ was postulated as coming from another CH_3CHBr group or radical and not from Br^- or Br_2 in the solution.

Since only these few electrolyses of

TABLE I

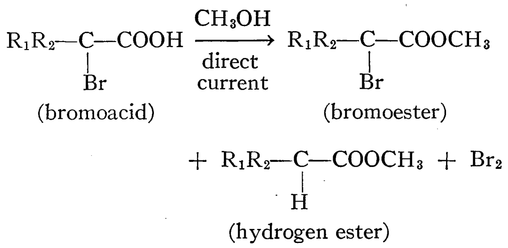
Electrolysis of α-bromocarboxylic acids in methanol solution

							Yield (%)			
							Neutral fraction		Acid fraction	
Acid used*	Solvent (ml)	Current (A)	Time (h)	Temp. (°C)	Weight of neutral fraction (g)	Weight of acid fraction (g)	Bromo-ester	Hydrogen ester	Bromo-acid	Hydrogen acid
α-Bromovaleric acid	25	0.4	3.7	37	3.71	0.30	28	54	6.0	0
	25	0.4	13	37	3.81	—	23	61	—	—
	25	0.4	28	37	3.71	—	16	68	—	—
	25	1.2	18	70	3.64	—	23	71	—	—
	25	0.6	12	40	7.72	—	30	51	—	—
α-Bromocaproic acid	30	0.5	5.5	38	7.07	0.94	34	46	8.6	1.1
	30	0.5	16	38	6.27	—	18	64	—	—
	30	0.5	41	38	6.23	—	14	69	—	—
	60	1.0	5.5	20	6.21	—	14	68	—	—
α-Bromodiethylacetic acid	25	0.5	5.0	35	6.28	0.45	15	61	1.4	5.2
	25	0.5	14	35	5.71	—	Trace	80	—	—
	25	0.5	28	35	6.12	—	Trace	87	—	—
	50	0.8	18	20	5.92	—	Trace	84	—	—
α-Bromoisobutyric acid	30	0.8	6.0	35	6.89	0.48	28	53	4.0	1.2
	30	0.8	12	35	6.52	—	25	59	—	—
	30	0.8	24	35	6.12	—	17	67	—	—
	60	1.0	6.0	20	6.22	—	19	64	—	—

*The first four experiments based on 5.0 g original acid; all others on 10.0 g.

α-haloacetic and α-halopropionic acids in water have been made, we decided to ascertain if their reactions were typical of α-haloacids in general. Four representative α-bromoacids were chosen, α-bromovaleric, α-bromocaproic, α-bromoisobutyric, and α-bromodiethylacetic acids and electrolysis reactions were carried out in methanol and water as solvents.[1]

The results of various electrolysis reactions of these α-bromoacids in methanol are summarized in Table I. The products are illustrated in the following equation (R_1 = alkyl, R_2 = alkyl or H).



$$\underset{\text{(bromoacid)}}{\mathrm{R_1R_2{-}\underset{\substack{|\\ Br}}{C}{-}COOH}} \xrightarrow[\text{direct current}]{\mathrm{CH_3OH}} \underset{\text{(bromoester)}}{\mathrm{R_1R_2{-}\underset{\substack{|\\ Br}}{C}{-}COOCH_3}} + \underset{\text{(hydrogen ester)}}{\mathrm{R_1R_2{-}\underset{\substack{|\\ H}}{C}{-}COOCH_3}} + \mathrm{Br_2}$$

Methanol is a common solvent in Kolbe electrolyses since the experimental conditions for optimum yield of dimer are often less critical than in aqueous media, even though some esterification usually occurs. Table I shows that the methyl bromoester and the methyl hydrogen ester were the only major organic products from the electrolysis of the α-bromoacids in methanol. No Kolbe dimer was found, nor were other possible products such as alcohols, ethers, and paraffins obtained. Considerable free bromine was produced in each case, but only at the anode. Methyl esters of an acid being electrolyzed have often been regarded as the result of attack of the initial carboxy radical on the methanol. Bunyan and Hey (16) suggested that at lower temperatures the carboxy radical is more stable, and attack on the solvent might take place in preference to loss of carbon dioxide and dimerization. In our work, changes of temperature or concentration appeared to have little effect, but as the time of electrolysis increased, the ratio of hydrogen ester to bromoester increased.

To get a clearer picture of the electrode processes involved, a series of small-scale experiments were run in a divided compartment cell. The use of a glass frit plus an agar plug allowed migration of inorganic ions such as Br^- but no migration of organic reactants or products. Products created at the cathode and anode were thus identified. Reduction of C—Br to C—H in both the ester and acid was shown to occur at the cathode only; bromide ion was liberated and in addition the cathode solution became more basic. Migration of Br^- to the anode and subsequent oxidation produced free bromine. These results indicate C—Br reduction occurs in the manner generalized by Elving and Pullman (18), wherein RX picks up two electrons to give R^- and X^-, and R^- abstracts a proton from solvent or in our case possibly from un-ionized acid. In some reductions, a two-step process $RX \rightarrow R\cdot + X^- \rightarrow R^- + X^-$ occurs, generating side products such as R—R from dimerization of R·. No such dimeric products were isolated in the α-bromoacid electrolyses, nor any other products indicative of radical involvement in the cathodic reduction process.

Divided cell electrolyses showed that esterification occurs reasonably rapidly at the anode only and the acidity of the anode solution increases as the reaction proceeds. Control experiments on esterification (with no electrolysis) showed that prolonged heating of the α-bromoacids or the unsubstituted acids in methanol produced little or no reaction. But small amounts of added H^+ produced considerable esterification even at room temperature; unsubstituted straight-chain acids were 50–60% esterified after 2 h and unsubstituted branched-chain acids about 20%. The bromoacids esterified at almost the same rate as their unsubstituted analogues, indicating very little effect of the α-bromo-substituent on the normal esterification process. Thus, a possible

---

[1] After this work was completed and during a revision of the manuscript, Annino *et al.* (17) published a study of the electroreduction of the carbon–bromine bond in 1-bromo-2,2-diphenylcyclopropanecarboxylic acid, its methyl ester, and 1-bromo-1-methyl-2,2-diphenylcyclopropane. Reduction of C—Br to C—H took place at a mercury cathode with the ester being somewhat easier to reduce than the acid. Although we used a smooth platinum cathode, the reductions occurring during α-bromoacid electrolyses appear to be similar.

explanation for the predominence of esterification in our original electrolyses is that esterification occurs at the anode surface or close to it, where the localized H^+ concentration is high and local heat effects are possible, and is mostly a normal acid-catalyzed reaction of carboxylic acid with methanol. Only ester and no Kolbe product is formed because the normal Kolbe reaction of $RCOO^- \rightarrow RCOO\cdot$ is relatively much slower with the bulkier, heavier bromine atom present[2] and not because esterification is faster with an α-bromo-substituent present. Solvent carries more than its normal share of the current and thus esterification becomes the predominant process. It is doubtful if much, if indeed any, of the ester is produced by reaction of $RCOO\cdot$ with methanol. Aliphatic $RCOO\cdot$ decarboxylates very rapidly and if present to form esters, it would be reasonable to expect products derived from decarboxylation to $R\cdot$ as well. Such products were not found.

A comparison of the separate electrode reactions showed that esterification at the anode is a more rapid process than C—Br reduction at the cathode, although the difference is less pronounced with the branched-chain acids where esterification is slower. This suggests that esterification of the bromoacid followed by reduction is the more important route to hydrogen ester, especially for the unbranched acids. Reduction of the bromoacid and then esterification does play an increased role with the branched-chain acids, but undoubtedly some reduction of both acid and ester occurs in all cases. No Kolbe dimer from the appropriate hydrogen acid was produced except from α-bromodiethylacetic acid where traces of 3,4-diethylhexane were found (electrolysis of diethylacetic acid under similar conditions gave only 11% of this dimer, which is typical of the suppression of Kolbe dimerization when an α-alkyl group is present).

To eliminate the formation of esters as major products, water was used as a solvent for further electrolysis studies. It was found that α-bromovaleric and α-bromocaproic acids (straight-chain acids) behaved differently from α-bromodiethylacetic and α-bromoisobutyric acids (branched-chain acids) in aqueous media, although free bromine was liberated in all cases. For the straight-chain acids, the electrolysis products were *n*-butyl bromide (25%), 1,1-dibromobutane (27%), and *n*-octane (17%) from α-bromovaleric acid and *n*-pentyl bromide (32%), 1,1-dibromopentane (27%), and *n*-decane (14%) from α-bromocaproic acid. The branched-chain acids produced ketones primarily. α-Bromodiethylacetic acid gave 3-pentanone (32%), 2-bromo-3-pentanone (29%), and 2,4-dibromo-3-pentanone (trace), whereas α-bromoisobutyric acid gave acetone (trace), bromoacetone (31%), 1,1-dibromoacetone (19%), 1,3-dibromoacetone (5%), and isobutyl bromide (trace).

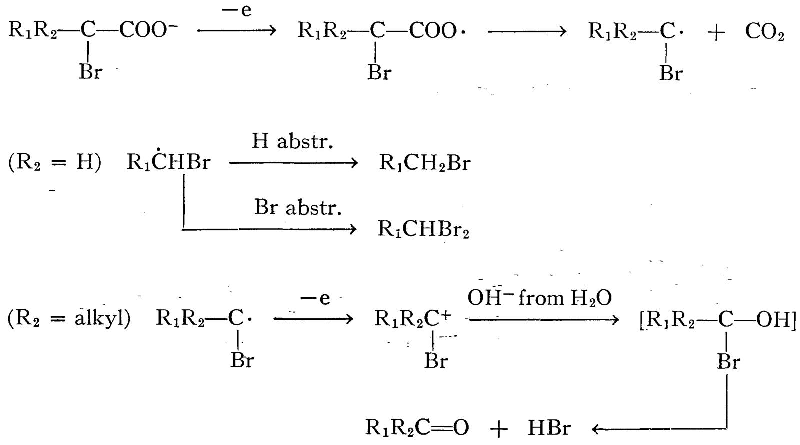
The presence of *n*-octane and *n*-decane in low yield in the electrolysis products of the two respective straight-chain acids show that, at least in part, the α-bromovaleric and α-bromocaproic acids were converted to hydrogen acids which gave the normal Kolbe dimer. Divided cell electrolyses in water solution showed that reduction at the cathode converted the α-bromoacids to unsubstituted acids very readily and that by migration of Br^- from the cathode to the anode, oxidation gave free bromine. Ketone products were created exclusively at the anode. Control experiments showed that, whereas C—Br reduction in the bromoacid occurs readily, there is only a very slight tendency for the bromide and dibromide products to be reduced under the experimental conditions used.

---

[2] Dr. Lennart Eberson, University of Lund, Sweden, has reviewed this manuscript and has suggested a *possible* alternate mechanism. Preliminary studies (not yet published) have been carried out by Dr. Eberson on anodic transesterification of ethyl half-esters in methanol and on anodic hydrolysis of methyl half-esters in aqueous dioxane. Coupled with polarographic studies indicating ethyl acetate can be oxidized anodically, these findings suggest that acyl-oxygen cleavage might occur at the anode with sterically hindered esters in a process that could be tentatively expressed as $RCOOR_1 \rightarrow RCO^+ + OR_1^+ + 2e$. If a similar process occurred with the α-bromoacids ($R_1 = H$), ester formation would result from attack of RCO^+ on methanol. This is a very interesting possibility and we thank Dr. Eberson for allowing us to mention it here.

It is reasonable to assume that the branched-chain acids yielded 3-pentanone and acetone as primary electrolysis products and subsequent bromination, either at the electrodes or from the free bromine in solution, gave the various bromoketones. Complete bromination of 3-pentanone did not occur, since it and the free bromine produced were not very soluble in the water solution, and in spite of the turbulence at the electrodes, most of the bromine collected in a layer at the bottom of the cell, while the 3-pentanone tended to float in a layer at the top. To confirm acetone as a primary product, an identical electrolysis of α-bromoisobutyric acid was run for only 8 h rather than 23. Acetone (14%) as well as a higher yield of bromoacetone (43%) and considerably lower yields of the dibromoacetones were obtained.

A possible explanation for the difference in product formation from straight-chain and branched-chain acids could be that both undergo a one-electron oxidation followed by loss of CO_2 to give the radical $R_1R_2—\dot{C}Br$. When $R_2 = H$, this radical reacts by hydrogen or bromine abstraction, but no further oxidation at the electrode occurs. When R_2 = alkyl, a second one-electron oxidation occurs to give the carbonium ion $R_1R_2—\overset{+}{C}Br$ which picks up OH^- from H_2O, and the ketone results. This second stage of oxidation is more reasonable when two alkyl groups are present to stabilize the carbonium ion and is consistent with previous carbonium ion production, which tends to be important with secondary or tertiary radicals rather than with primary radicals.



$$R_1R_2—\underset{\mathrm{Br}}{\underset{|}{C}}—COO^- \xrightarrow{-e} R_1R_2—\underset{\mathrm{Br}}{\underset{|}{C}}—COO\cdot \longrightarrow R_1R_2—\underset{\mathrm{Br}}{\underset{|}{C}}\cdot + CO_2$$

$$(R_2 = H)\quad R_1\dot{C}HBr \xrightarrow{\text{H abstr.}} R_1CH_2Br$$
$$R_1\dot{C}HBr \xrightarrow{\text{Br abstr.}} R_1CHBr_2$$

$$(R_2 = \text{alkyl})\quad R_1R_2—\underset{\mathrm{Br}}{\underset{|}{C}}\cdot \xrightarrow{-e} R_1R_2\underset{\mathrm{Br}}{\underset{|}{C}}{}^+ \xrightarrow{OH^-\text{ from }H_2O} [R_1R_2—\underset{\mathrm{Br}}{\underset{|}{C}}—OH] \longrightarrow R_1R_2C{=}O + HBr$$

The possibility that other processes may also be involved cannot be disregarded. For example, bromine abstraction by the radical derived from the hydrogen acid would also explain alkyl bromide formation.

The work described represents the first detailed study of the electrolysis of a number of α-bromoacids in both methanol and aqueous media. Although only four acids were studied, the results appear likely to represent a general behavior for such compounds. No Kolbe dimer was produced, even in small amounts. We hope to study further the electrolyses of α-bromoacids in other solvents to see if conditions for dimer formation can be found.

EXPERIMENTAL

The bromoacids were obtained from Eastman Organic Chemicals, Rochester, New York, or Sapon Laboratories, Lynbrook, New York, and were redistilled before use. As shown by gas–liquid chromatography (g.l.c.), purity of better than 99.8% was obtained; the major impurity was the hydrogen acid, which could not be completely removed by repeated distillations. Boiling points are uncorrected. The g.l.c. analysis and separation were carried out on an Aerograph Autoprep model 700 with a 10 ft × 3/8 in. column with 30% loading of either silicon gum rubber SE-30 or Carbowax 20M. For both, the column support was 60/80 mesh Chromosorb W. Temperature programming was used in the range 140–250°. Detector temperature was kept ca. 25° above the column temperature when collection of the sample was needed. Infrared spectra were taken with Beckman IR–5 and IR–10 spectrophotometers on thin liquid films. Nuclear magnetic resonance (n.m.r.) spectra were obtained with a C-60 chemical analyzer JEOL spectrometer. Microanalyses were obtained from Schwarzkopf Microanalytical Laboratory, Woodside, New York.

The conventional electrolysis cell, general method of electrolysis, and isolation of products have been described before (19). All of the large-scale electrolyses in water and methanol were run in this cell. When water was the solvent, neutralization of 40% of the acid was necessary to produce sufficient current. Yields of bromine liberated were in the range 8–23% and were determined by distilling the bromine from a steam bath, bubbling it into silver nitrate solution, and collecting the silver bromide precipitated.

The divided cell experiments in both methanol and water are described at the end of this Experimental section.

Electrolyses of α-Bromoacids in Methanol

The results of these electrolyses are found in Table I. The esters were obtained by distillation of the neutral fraction. They were identified by comparison of physical constants with literature values, with infrared (i.r.) spectra, which were as expected, and by comparison with authentic esters, especially in their g.l.c. behavior. Methyl α-bromodiethylacetate was a new compound having b.p. 184.5–186° (740 mm), n_{D}^{17} 1.4626, and major i.r. absorption (cm^{-1}) at 1 762 (C=O), 1 157 (C—O—CH$_3$), and 655 (C—Br).

Anal. Calcd. for $C_7H_{13}O_2Br$: C, 40.22; H, 6.27; Br, 38.22. Found: C, 40.41; H, 6.45; Br, 38.21.

For comparison, certain control reactions were run. Electrolysis reactions carried out on samples of the appropriate methyl esters under similar conditions to those shown in Table I gave similar relative yields of bromo and hydrogen esters. Prolonged heating of the methyl esters with no passage of current produced no conversion to hydrogen ester. Prolonged heating of the α-bromoacids under electrolysis conditions, but with no current, gave no conversion to hydrogen acid but did produce some (ca. 10%) esterification to the appropriate methyl α-bromoester. Esterification did occur with added H$^+$ as discussed before.

Electrolysis of α-Bromovaleric and α-Bromocaproic Acids in Water

Potassium hydroxide (6.3 g, 0.112 mole) was dissolved in water (80 ml) and α-bromovaleric acid (50.0 g, 0.276 mole) was added. A current of 1.2 A was passed for 37 h and the temperature was kept at ca. 17° with an ice bath. The color of the solution changed to deep red during electrolysis and a layer of bromine separated. After isolation of neutral and acidic fractions in the usual manner, a light-brown neutral oil (22.5 g) was collected, which gave three fractions on microdistillation (740 mm). After two more distillations, the first two fractions gave *n*-butyl bromide (9.5 g, 25%), b.p. 102–103°, n_{D}^{20} 1.4393 (lit. b.p. 101° (768 mm), n_{D}^{20} 1.4399 (20)) and *n*-octane (2.7 g, 17%), b.p. 124–125°, n_{D}^{20} 1.3978 (lit. b.p. 124.5° (760 mm), n_{D}^{20} 1.3974 (21)). These fractions showed the same g.l.c. behavior and i.r. spectra as authentic samples. The third fraction (8.1 g, b.p. 160–168°) contained 1,1-dibromobutane and traces of some unidentified components. Redistillation gave b.p. 161–162.5°, $n_{\mathrm{D}}^{18.5}$ 1.5020 (lit. b.p. 72° (43 mm), n_{D}^{25} 1.4980–1.4989 (22)). The 8.1 g obtained represented a 27% yield, calculated on the basis of 2 moles of bromoacid yielding 1 mole of dibromide, since the bromoacid was the only initial source of bromine. A small sample of this dibromide (0.83 g) was isolated with the Autoprep–700 using the Carbowax 20M column, temperature programming from 150–180°, and a detector temperature of 200°. The i.r. spectrum showed strong absorption at 665 cm^{-1} (CHBr$_2$).

Similarly α-bromocaproic acid (48.0 g, 0.246 mole) was electrolyzed at 1.5 A for 26 h. The first two distillation fractions, whose identities were also confirmed by comparison with authentic compounds, were *n*-pentyl bromide (11.9 g, 32%), b.p. 127–128.5°, n_{D}^{22} 1.4443 (lit. b.p. 128.5° (764 mm), n_{D}^{20} 1.4450 (20)) and *n*-decane (2.37 g, 14%), b.p. 172–173.5°, n_{D}^{23} 1.4107 (lit. b.p. 172.5° (762 mm), n_{D}^{20} 1.4121 (21)). 1,1-Dibromopentane (7.52 g, 27%) was isolated by two distillations followed by g.l.c. using the Carbowax 20M column, temperature programming from 170–190°, and a detector temperature of 220°. This dibromide had b.p. 181–182°, n_{D}^{26} 1.4916.

Anal. Calcd. for $C_5H_{10}Br_2$: C, 26.16; H, 4.42; Br, 69.30; Found: C, 26.12; H, 4.38; Br, 69.50.

The i.r. spectrum showed strong absorption at 665 cm^{-1} (CHBr$_2$). The n.m.r. spectrum showed four groups of peaks at τ = 4.3, 8.3, 8.6, and 9.1 with relative intensities of 1:2:4:3. The triplet at τ = 4.3 (J = 6.3 c.p.s.) arose from the hydrogen of the —CHBr$_2$ group. The symmetry of the n.m.r. spectrum, the chemical shifts, and the multiplicities agree with the expected spectrum of 1,1-dibromopentane.

Electrolysis of α-Bromodiethylacetic and α-Bromoisobutyric Acids in Water

α-Bromodiethylacetic acid (50.0 g, 0.257 mole) was added to a cooled solution of potassium hydroxide (5.8 g, 0.104 mole) in water (80 ml). 1.5 A were passed for 23 h and the temperature was kept at 20–25° with an ice bath. Bromine evolution took place as described above. Distillation of the neutral product (25.9 g) gave two main fractions, the first of which was 3-pentanone (8.8 g, 32%), b.p. 101–102.5°, n_{D}^{23} 1.3913 (lit. b.p. 102° (751 mm), n_{D}^{20} 1.3922 (23)). The i.r. spectrum showed strong absorption at 1 710 cm^{-1} (C=O), and i.r. and g.l.c. behavior was identical with an authentic sample. Gas–liquid chromatography showed that 2-bromo-3-pentanone (12.2 g, 29%) was the major component of the second fraction, together with a trace of

2,4-dibromo-3-pentanone (confirmed by use of an authentic sample (24)). 2-Bromo-3-pentanone was purified further with the Autoprep–700 using the SE-30 column and temperature programming from 150–200° and had b.p. 44–46° (13 mm), n_D^{25} 1.4560 (lit. b.p. 48° (12 mm), n_D^{25} 1.4560 (25)). The i.r. spectrum showed strong C=O absorption at 1 727 cm^{-1}. The n.m.r. spectrum showed four groups of peaks at $\tau = 5.2$, 6.9, 8.1, and 8.8 with relative intensities of 1:2:3:3. The spectrum was in accord with the proposed structure and identical with the n.m.r. spectrum of an authentic sample and with a previously published spectrum of this bromoketone (26).

Similarly α-bromoisobutyric acid (40.0 g, 0.240 mole) was electrolyzed at 1.5 A for 30 h. Gas–liquid chromatography showed mainly bromoacetone and traces of acetone and isopropyl bromide in distillation fraction I of the neutral product. Two redistillations gave bromoacetone (10.2 g, 31%), b.p. 135.5–137°, $n_D^{21.5}$ 1.4747 (lit. b.p. 38–39° (11 mm), n_D^{25} 1.4739 (25)). The i.r. spectrum showed C=O absorptions at 1 727 and 1 746 cm^{-1}. By comparison with authentic 1,1-dibromoacetone and 1,3-dibromoacetone (27), g.l.c. showed the presence of both these dibromoketones in distillation fraction II (b.p. 150–185°). 1,1-Dibromoacetone (4.91 g, 19%) was isolated with the Autoprep–700 using the SE-30 column and temperature programming of 150–200° and had $n_D^{20.5}$ 1.5267 (lit. n_D^{25} 1.5237 (25)); it showed C=O absorptions at 1 720 and 1 745 cm^{-1} and $CHBr_2$ absorption at 667 cm^{-1}. Because of the small amount of 1,3-dibromoacetone (5%, calcd. from g.l.c.), isolation was not possible.

Divided Cell Electrolyses

The bromoacids (4 g scale) were electrolyzed for periods of up to 12 h in methanol and water under conditions closely paralleling those of the previous experiments but in an H-shaped cell with separate electrode compartments, each of 25 ml capacity. A glass frit of 1 cm diameter and a 2 cm agar plug of the same diameter separated the compartments. The agar plug had to be replaced every 2 h during long electrolyses to ensure no migration of organic substances. Platinum foil electrodes 0.5 × 1.0 cm were used at a separation of 4 cm. The temperature of reaction was 15–20° in water and 20–25° in methanol at currents of 0.2 and 0.08 A respectively. Comparisons of the reaction rate in each compartment were made by g.l.c. analysis of aliquot samples withdrawn at periodic intervals. The behavior of the bromoesters and other products was studied. The production of bromine at the *anode* was observed with an anode compartment of pure solvent and a cathode solution of sodium bromide in that solvent. The results of all these divided cell experiments have been discussed earlier.

ACKNOWLEDGMENTS

We are indebted to the National Research Council of Canada for financial assistance and to Dr. T. E. Gough of this Department for assistance with the n.m.r. spectra. We are also extremely grateful to Dr. Lennart Eberson, University of Lund, Lund, Sweden, for helpful suggestions on the divided cell electrolyses and for constructive criticism of the manuscript.

REFERENCES

1. R. G. WOOLFORD and W. S. LIN. Can. J. Chem. **44**, 2783 (1966).
2. R. P. LINSTEAD, B. R. SHEPHARD, and B. C. L. WEEDON. J. Chem. Soc. 2854 (1951).
3. M. FINKELSTEIN and R. C. PETERSON. J. Org. Chem. **25**, 136 (1960).
4. B. C. L. WEEDON. Advan. Org. Chem. **1**, 1 (1960).
5. L. EBERSON. Acta Chem. Scand. **17**, 2004 (1963).
6. L. EBERSON. Acta Chem. Scand. **13**, 40 (1959).
7. L. EBERSON. Acta Chem. Scand. **14**, 641 (1960).
8. L. EBERSON. J. Org. Chem. **27**, 2329 (1962).
9. L. EBERSON. Acta Chem. Scand. **17**, 1196 (1963).
10. F. SWARTZ. Bull. Soc. Chim. Belges, **42**, 102 (1933).
11. B. E. CONWAY and M. DZIECIUCH. Proc. Chem. Soc. 121 (1962).
12. J. TROEGER and E. EWARS. J. Prakt. Chem., Ser. 2, **58**, 127 (1898).
13. F. KAUFLER and C. HERZOG. Ber. **42**, 2870 (1909).
14. K. ELBS and K. KRATZ. J. Prakt. Chem. **55**, 502 (1897).
15. G. W. THIESSEN and R. MILLER. J. Am. Chem. Soc. **77**, 770 (1955).
16. P. J. BUNYAN and D. H. HEY. J. Chem. Soc. 1360 (1962).
17. R. ANNINO, R. E. ERICKSON, J. MICHALOVIC, and B. MCKAY. J. Am. Chem. Soc. **88**, 4424 (1966).
18. P. J. ELVING and B. PULLMAN. Advan. Chem. Phys. **3**, 1 (1961).
19. R. G. WOOLFORD. Can. J. Chem. **40**, 1846 (1962).
20. A. I. VOGEL. J. Chem. Soc. 637 (1943).
21. A. I. VOGEL. J. Chem. Soc. 133 (1946).
22. J. C. CONLY. J. Am. Chem. Soc. **75**, 1148 (1953).
23. D. M. COWAN, G. H. JEFFREY, and A. I. VOGEL. J. Chem. Soc. 171 (1940).
24. C. RAPPE and L. SCHOTTE. Acta Chem. Scand. **16**, 2060 (1962).
25. C. RAPPE and R. KUMAR. Arkiv Kemi, **23**, 475 (1965).
26. C. RAPPE. Arkiv Kemi, **21**, 503 (1963).
27. E. D. HUGHES, H. B. WATSON, and E. D. YATES. J. Chem. Soc. 3318 (1931).