THE KOLBE ELECTROCHEMICAL SYNTHESIS: AN ACADEMIC TOPIC

GARRETT W. THIESSEN
Monmouth College, Monmouth

The electrolysis of organic-acid salts initiated by Kolbe in 1849 remains one of the most direct approaches to the study of free radicals. The concentrated potassium acetate which he first used is excellent for demonstrating this experiment. This solution is made by saturating water with solid potassium acetate and adding about five percent of the volume of glacial acetic acid. It is both anolyte and catholyte. The cathode is copper wire gauze. The anode is platinum foil, secured through a rubber stopper in a porous cup. A glass tube through this stopper permits the gaseous products of the electrolysis to escape from the reaction chamber. They pass through a U tube containing glass beads and 6 N. aqueous NaOH solution, then through another U tube containing glass beads and conc. H_2SO_4; thence they are led to a pneumatic trough for collection. Neither dimensions of the apparatus nor concentrations of the solutions are critical. Also the electrolyzing voltage may vary within rather wide limits. It may be as little as 8 volts or even less if the experiment may be started some hours ahead of class time; but if 15 to 20 volts[1] are available, the experiment may be started with the start of the lecture, and will in a few minutes yield sufficient ethane for a burning test. It is one of the few organic chemistry experiments well-adapted for lecture demonstration.

To interpret it from the free-radical viewpoint is a fine exercise in visualization of molecular behavior. The starting material is acetic acid; the products are cathodic hydrogen, and anodic carbon dioxide and ethane, mainly; though some ethylene, methanol, and methyl acetate are also formed at the anode. The following sequence of events is presumed to explain these results:

(a) Before electrolysis—ionization of solvent and salt, the former only slight.

(b) At cathode—arrival of cations K^+ and H_3O^+, with selective discharge of latter (see activity series) with production of H_2.

(c) At anode—arrival of anions $CH_3 \cdot COO^-$ and OH^-, with selective discharge mainly, but not exclusively, of the former, producing the free radicals $CH_3 \cdot COO$ and OH[2]. Each of these contains an odd number of electrons.

(d) Decomposition of some $CH_3 \cdot COO$ into CH_3 and CO_2, (and some OH into O_2 and H_2O). The new free radical thus formed contains also an odd number of electrons.

(e) The formation of all possible stable combinations of the three free radicals present. The radicals are (1) $CH_3 \cdot COO$, (2) CH_3, (3) OH. The stable products predicted and found are: $CH_3 \cdot CH_3$, $CH_3 \cdot COO \cdot CH_3$, and CH_3OH, besides the CO_2. In the demonstration, the NaOH in

---

[1] External cooling is advisable with higher voltages.

[2] The $CH_3.COO.OOC.CH_3$ and HO.OH postulated as intermediates in current theories of this synthesis would be in equilibrium, theoretically, with the two prime free radicals.

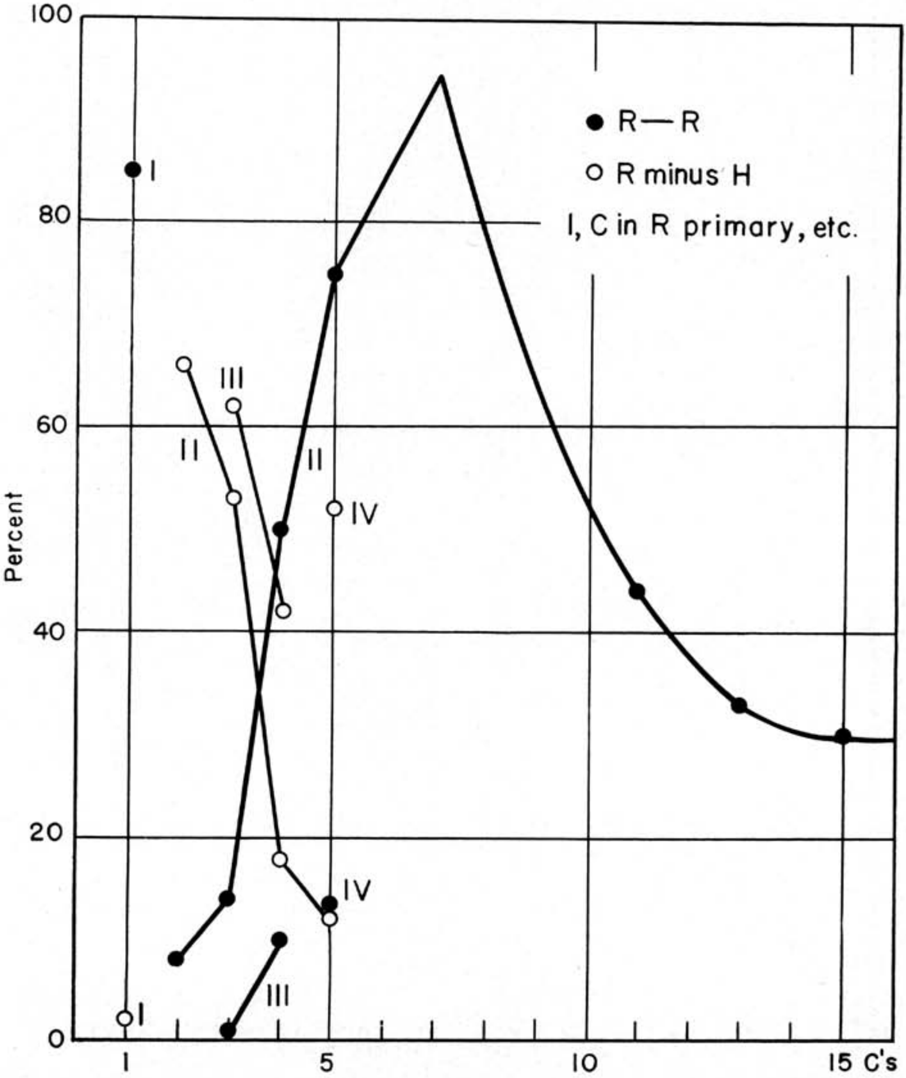

FIG. 1.—Current yields vs. number of C's in R.

the first U tube removes the CO_2. All the stable products have even numbers of electrons.

(f) The loss of H atoms from some of the CH_3 radicals. Since each H atom carries an electron, this leaves the new CH_2 radical with an even number of electrons, so it is a reaction which should tend to occur. The methylene dimerizes to C_2H_4, which is removed from the ethane by the H_2SO_4 in the second U tube.

It is also helpful to visualize this electrolysis of acetic acid in relation to two very familiar pyrolyses of the same substance. Thus,

(a) acetate ion + alkali ion + thermal energy → methane + carbonate.

(b) acetate ion + alkali ion + electrical energy → ethane + carbon dioxide + hydroxide ion (formed at cathode when H_2 is liberated).

(c) acetate ion + alkaline-earth ion + thermal energy → acetone + carbonate.

Since, of course, the carbonate or hydroxide can be converted to the starting salt by adding more acetic acid, with evolution of CO_2 if the carbonate was formed, all three processes are decarboxylations of acetic acid; and the effect of the different metals, together with the directive action of the electrical field, may be compared as a study in catalysis.

Further, the Kolbe synthesis is the basis of interesting speculation. By analogy to the first example, $R \cdot COOK$ should yield $R \cdot R$ abundantly, whatever the nature of $R \cdot$, with a little (R minus H), ROH, and $R \cdot COO \cdot R$. This is not true. Even when R contains nothing but C and H, and is saturated, the proportions of the products are highly variable. Thus, potassium propionate yields very little n-butane, but produces ethylene (R minus H) copiously. As the homologous series is pursued, results intermediate between these two extremes appear. This is shown graphically in figure 1, in which the number of carbon atoms in R is plotted against percent current[3] yield. (The data here plotted are taken from table VIII, p. 43 of item (2) of the bibliography.) Solid circles designate $R \cdot R$; open circles (R minus H). The roman numbers designate the type of carbon atom attached to the carboxyl group. In acetic acid, it is primary (I), being attached to only one other carbon. In the straight-chain acids propionic to stearic,[4] it is secondary (II). For this series most data were available. Only a pair of tertiary acids were tabulated, and only one quaternary. The following generalizations can be deduced from figure 1:

(a) The yield of $R \cdot R$ is an inverse function of the yield of (R minus H).

(b) The type of carbon atom attached to the carboxyl determines the family to which an acid belongs in this synthesis.

(c) The extra CH_2 group acquired in converting a secondary carbon atom to a tertiary does not greatly alter the yield, since curves III could nearly be superimposed on curves II by shifting the abscissa one unit to the left.

(d) The maximum yield of $R \cdot R$ might be expected in about the

---

[3] The current yield is chosen rather than the material yield because it is more easily defined. This is because the cathode action forms ions equivalent to KOH in its vicinity, and the solution tends to become alkaline as electrolysis progresses; and when the hydroxide ion concentration reaches the anode, hydroxide discharges ever more readily and production of $CH_3.COO$ radicals falls off. To prevent this, excess of the free acid whose potassium salt is being electrolyzed is maintained in the system.

[4] Off the scale of figure 1, but on the curve,

region of octanoic acid, where the data fail.

(e) Acetic acid is an isolated, rather than a typical, case.

(f) The production of (R minus H) is about as typical as the production of R · R.

More speculation may be centered about the role of unsaturation in this synthesis. As a product, it is common. When it is initially present, it inhibits the synthesis. It does this by raising the discharge potential of the organic anion, making it relatively easier to discharge hydroxyl. Straight-chain double bonds, if nearer to the carboxyl than the delta atom, usually prevent the synthesis from occurring. Benzenoid double bonds have a similar action. Fichter and Stenzl used pyridine, alone or with methyl alcohol, as a solvent for this synthesis, and thus provided solvent anions much more difficult to discharge than hydroxyl. In these solvents they were able to convert benzoic acid to diphenyl, and phenylacetic acid to dibenzyl.

It is interesting to note that some 4-phenylpyridine was recovered in the electrolysis of benzoate in pyridine. This is for this system analogous to ROH in water, and suggests that pyridine ionizes by disengaging a hydrogen atom at the point most remote from the nitrogen, and that if other ions are also produced, this is the one most easily discharged. As a rough approximation, unsaturation is a fairly typical product; its initial presence operates against the formation of more, according to Le Chatelier's theorem.

Since the ethylenic double bond is a ring system of two atoms, the behavior of larger ring systems is of interest. Such systems with three, four, and five carbon atoms in the ring, and the ring adjacent to the carboxyl group, have been investigated. Only R · COO · R and ROH seem to evolve in significant amounts. This suggests: (a) the organic discharge potential is somewhat raised, so that it is about comparable to that of hydroxide, so that liberal amounts of both R · COO and OH are present together; (b) the rate of decomposition of R · COO into R and CO_2 is lowered, so that considerable R and R · COO exist together.

Finally, the synthesis offers a wide field for investigation. Decomposition potentials, material yields, and gas analyses are largely unrecorded, except for the first three members. Other solvents besides pyridine, methyl alcohol, and water might be investigated. The effect of the alicyclic ring more remote from the carboxyl appears to be unknown. The effects of temperatures and pressures much greater than atmospheric have not been studied. Much may possibly be done by a careful literature search; the earliest work is so old that copies or direct abstracts of it are not available in the smaller chemical libraries. For many experimental studies no especially difficult apparatuses or techniques are needed. A study of the electrolysis of mandelate ion, $C_6H_5 \cdot CHOH \cdot COO^-$, is offered as an example. Since this is a substituted acid, it might be well to note these recorded results for such; R is listed:

(a) Forms R · R · abundantly: acetyl, o-nitrophenyl.

(b) Forms (R minus H) abundantly: α-hydroxy ethyl, α-hydroxy proply, β-hydroxy propyl, ∂-gluconyl, allo-camphoryl, phenyl hydroxy methyl (which is the R of the mandelate ion).

The case of R being $C_6H_5 \cdot CHOH$ was investigated by Walker in 1896, using an aqueous solution.[5] He records the production of only small amounts of hydrobenzoin $C_6H_5 \cdot CHOH \cdot CHOH \cdot C_6H_5$, but a considerable amount of benzaldehyde, C_6H_5CHO. Since the former is the RR product and the latter is (R minus H), it is evident that mandelic acid, $C_6H_5 \cdot CHOH \cdot COOH$, resembles propionic acid rather than acetic acid in regard to behavior of its ion in a Kolbe electrolysis. Walker suspected that the hydrobenzoin resulted from the cathodic reduction of the benzaldehyde. It is, of course, possible to take the converse view and assume that the benzaldehyde results from the anodic oxidation of the hydrobenzoin. Oxygen thus used would come from discharged hydroxyl ions from the solvent water. This proposition was tested by using the technique of Fichter and Stenzl to electrolyze the mandelate ion in non-aqueous solvent. The potassium salt in methanol-pyridine, and the diethylammonium salt in pure pyridine, were both tried.

An undivided cell was used. A small copper beaker held the electrolytic solution and served as a cathode. A platinum anode was supported by a glass tube led through a three-hole rubber stopper into the cell. Gas was led to a Burrell analyzer from a tube inserted in another bore of the stopper. The temperature of the mixture was maintained at 24°C. by external cooling with ice water. A typical reaction mixture was 51 ml. of 1 N. methanolic potassium hydroxide, 38 gms. of mandelic acid, and 51 ml. of pyridine. About 40 volts were used to maintain about 0.7 amperes of current. When a gas analysis was not desired, a larger electrolysis vessel, consisting of a 400 ml. tall-form beaker, was used. A spiral copper tube carrying water was the cathode, and a rotating platinum spiral was the anode. Coulombs would be passed in excess of the theoretically required amount. Several runs from the large cell would be combined for isolation of the organic products, by usual techniques, substantially as outlined by Fichter and Stenzl. Again much benzaldehyde was found, and very little hydrobenzoin. That some of the latter was present was proved by the precipitation of silver iodate from a solution of silver ions and periodic acid, a test quite specific for 1, 2 dialcohols. Moreover, by working up the material from the proper point in the organic separation scheme, a small amount of substance was prepared by reaction with benzoyl chloride, which gave the proper melting point for the dibenzoate of hydrobenzoin. Since pyridine alone gave no appreciable amount of hydrobenzoin, and since pyridine could not possibly release anode oxygen since it contains none, it could not be argued that the benzaldehyde resulted from the oxidation of the hydrobenzoin. Rather, the prime stable compound formed from the free radicals was of the (R minus H) type.

The average of several gas-analysis experiments was expressed as a ratio of H_2 to CO_2 equal to 0.8, the individual values varying from 0.763 to 1.075. Remembering that both cathodic and anodic H_2 is registered and that 2 faradays make 1 gram-molecular volume of cathodic hydrogen and 2 g.m.v. of anodic CO_2, we see that this ratio should be

---

[5] It is surprising that $C_6H_5 \cdot CHOH \cdot COO-$ ion discharges in aqueous electrolysis, since $C_6H_5 \cdot CH_2 \cdot COO-$ does not. Apparently, although the double bonds in the molecule tighten the terminal electron, the hydroxyl oxygen loosens it.

0.500 for a perfect RR synthesis; but if each radical that furnished a CO_2 furnished addionally $\frac{1}{2}H_2$, the ratio should be 1.00. Also, any discharge of solvent anions would increase this ratio by cutting down its denominator more extensively than the numerator. The picture supported by the gas analysis therefore is that of extensive (R minus H) synthesis, accompanied by some R · R formation.

BIBLIOGRAPHY

(1) Löb and Lorentz, *Electrochemistry of Organic Compounds*, Wiley, 1905.

(2) Brockman, *Electro-Organic Chemistry*, Wiley, 1926.

(3) Weissberger-Swann, *Technique of Organic Chemistry: Electrolytic Reactions*, Interscience, 1948.

(4) Ralston, *Fatty Acids and Their Derivatives*, Wiley, 1948, pp. 877-8.