

Studies on the Kolbe Electrolytic Synthesis

V. An Electrochemical Analogue of the Ritter Reaction

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It is now recognized that the main side reaction in the Kolbe electrolytic synthesis is the oxidation of the initially produced radicals to carbonium ions.¹⁻³ Theoretical calculations⁴ indicate that this reaction should be dependent upon the ionization potential of the radical and that carbonium ions should be formed dominantly in the electrolysis of acids RCOOH where R· has an ionization potential lower than about 8 eV. As an example of how electrolytically generated carbonium ions may be utilized for preparative purposes, we wish to report the transformation of an acid RCOOH into R-NHCOCH₃ by carrying out the electrolysis in acetonitrile.

The Ritter reaction⁵ is a method for the preparation of N-alkylacetamides from an alkene or an alcohol, acetonitrile and concentrated sulfuric acid. It seems probable that the mechanism involves an attack of a carbonium ion on the free electron pair of the nitrile group, a situation which should be duplicated during electrolysis of an acid RCOOH in acetonitrile, if R corresponds to an easily oxidized radical.

When trimethylacetic acid was electrolyzed in acetonitrile containing a few per cent of water, N-tert-butylacetamide could be isolated in 40 % yield, with no sign of formation of any coupled product. Now the synthesis of simple N-tert-alkylacetamides can be accomplished from cheap starting materials by non-electrolytic methods, so this synthesis has no special practical interest. On the contrary, for acids containing functional groups sensitive towards sulfuric acid and with structures corresponding to difficultly accessible olefins or alcohols the electrolytic method should be useful. As an example the electrolysis of monomethyl tetramethylsuccinate in acetonitrile gave a 25 % yield of the methyl ester of N-acetyl-2,2,3,3-tetramethyl-β-alanine, *i.e.* a derivative of a hitherto unknown amino acid.

These two examples suffice to show that it is possible to trap electrolytically produced carbonium ion by acetonitrile; studies on the preparative utilization of this method are under way.

Preparation of N-tert-butylacetamide. The electrolyte consisted of trimethylacetic acid (0.3 mole), potassium hydroxide (0.05 mole), acetonitrile (150 ml), and water (about 3 ml). It was electrolyzed between two Pt electrodes in a 200 ml water-jacketed beaker, equipped with a stirrer. The initial current was about 1 A (voltage 180 V) but fell gradually to about 0.2 A during the electrolysis. The temperature was kept below 40° by circulating tap water through the water jacket. After 16 h the reaction was stopped and some potassium bicarbonate formed was filtered off. The acetonitrile was then evaporated and the residue treated with 30 ml of petroleum ether (b.p. 40–60°). The solid was filtered and had m.p. 98–99° after one recrystallization from water. The yield was 14.0 g (40 %) and the compound was shown to be identical with an authentic specimen by v.p.c., infra-red spectra and mixed melting points.

Preparation of the methyl ester of N-acetyl-2,2,3,3-tetramethyl-β-alanine. The electrolyte consisted of methyl hydrogen tetramethylsuccinate (0.1 mole), potassium hydroxide (0.05 mole), acetonitrile (150 ml) and water (2 ml). The electrolysis was carried out as described above at a current of 0.5 A and at a temperature below 40°. After 11 h the electrolysis was stopped, the reaction mixture filtered, and the acetonitrile evaporated. Water was added to the residue and the organic material was taken up in ether. The ether solution was washed with aqueous sodium carbonate solution and water and the ether was distilled off. The residue was treated with petroleum ether, whereby crystals deposited. The crystal mass was filtered, dried, and recrystallized from petroleum ether. The yield of pure ester was 4.7 g (25 %), m.p. 90–91°. The infra-red spectrum showed the presence of an N-H bond, an amide and an ester group. The NMR-spectrum had signals (referred to tetramethylsilane) at $\tau = 4.1$ (very broad), 6.68, 8.27, 8.53, and 8.91 with integrated band areas in the proportions 0.2:1:1:2:2, with no spin-spin couplings. Assignments: $\tau = 4.1$ amide H; 6.68 ester CH₃; 8.27 acetyl CH₃; 8.53 CH₃ β to CH₃CONH-; 8.91 CH₃ β to -COOCH₃. (Analysis: Found: C 59.5; H 9.2; N 7.1; O 23.7. Calc. for C₁₀H₁₉NO₃: C 59.7; H 9.5; N 7.0; O 23.9).

A small sample of the methyl ester was hydrolyzed by boiling with an excess of ethanolic potassium hydroxide over night. The ethanol was distilled off and the residue acidified with 10 % hydrochloric acid. The solid was filtered off, dried, and recrystallized from ethyl acetate. According to analyses and infra-red spectrum it was N-acetyl-2,2,3,3-tetramethyl- β -alanine, m.p. 180–183°. (Analysis: Found: C 57.4; H 9.0; N 7.5; O 25.8. Calc. for $C_9H_{17}NO_3$: C 57.7; H 9.2; N 7.5; O 25.6).

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VI. On the Mechanism of Anodic Acetoxylation

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In paper IV of this series,¹ it was suggested that the formation of acetoxy compounds during electrolysis of sodium acetate in acetic acid in the presence of aromatic substrates (e.g. *o*- and *p*-acetoxyanisole from anisole² and 1-acetoxynaph-

Table 1. Oxidation half-wave potentials for some aromatic compounds in acetic acid containing 0.5 M sodium acetate.

Compound	$E_{1/2}$ in acetic acid versus s.c.e., trile ⁴ (0.5 M in corrected for $NaClO_4$) versus IR-drop in the Ag^+/Ag solution	$E_{1/2}$ in acetonitrile versus s.c.e., trile ⁴ (0.5 M in corrected for $NaClO_4$) versus IR-drop in the Ag^+/Ag solution
Anthracene	1.20	0.84
Acenaphthene	1.36	1.11
<i>Trans</i> -stilbene	1.51	
1,1-Diphenyl ethylene	1.52	
Retene	1.64	1.18
Fluorene	1.65	1.25
Anisole	1.67	1.35
Phenanthrene	1.68	1.23
Naphthalene	1.72	1.31
Diphenyl	1.91	1.48

thalene from naphthalene³) might occur by way of anodic oxidation of the aromatic substrate followed or assisted by reaction with acetate ion. The mechanism proposed earlier,² involving a homolytic reaction of electrolytically generated acetoxy radicals with the aromatic compounds, seems less attractive in view of the extremely short life-time of the acetoxy radical.

We now wish to report some preliminary results which show that the first mechanism must be the correct one. Lund⁴ and Pysh and Yang⁵ have determined the oxidation half-wave potentials in acetonitrile for a large number of aromatic compounds at a rotating platinum anode. It was found that acetic acid containing 0.5 M sodium acetate was also suitable as a medium for this type of oxidation polarography. In Table 1 values of $E_{1/2}$ (ox) versus the saturated calomel electrode (s.c.e.) for some compounds of interest are given, together with Lund's values in acetonitrile. There is a reasonably good linear correlation between these two sets of values.

Now the main point of interest in Table 1 is the value of $E_{1/2}$ for anisole and naphthalene, both of which are known to give acetoxy compounds when co-electrolyzed with acetate-acetic acid. Since the Kolbe process starts at potentials above 2.0 V vs. s.c.e.⁶ and does not occur at lower potentials, it is apparent that these two compounds are involved in an oxidation process at considerably lower potentials than