CLEAVAGE OF ESTER BONDS BY SOLVATED ELECTRONS GENERATED ELECTROCHEMICALLY IN HEXAMETHYLPHOSPHOROTRIAMIDE

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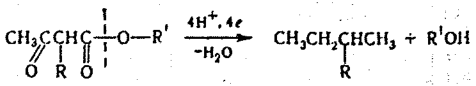
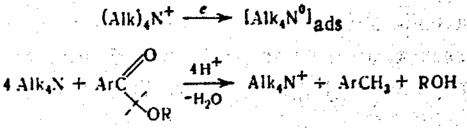
The ester bonds in ester molecules undergo electrolytic reduction only with difficulty. Tafel [1] was the first to establish that acetoacetic-acid esters and their homologs can be reduced to hydrocarbons in strongly-acid solution at a lead cathode:



$$CH_3\underset{O}{C}\underset{R}{C}H\underset{O}{C}-O-R' \xrightarrow[-H_2O]{4H^+,\,4e} CH_3CH_2\underset{R}{C}HCH_3 + R'OH$$

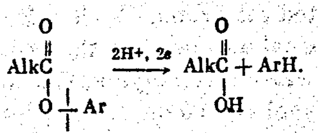
Much later, Horner [2] showed that aromatic-acid esters both with alkyl and with aryl-ester residues undergo reduction in methanol solutions containing a tetraalkylammonium salt as electrolyte. The hypothesis was expressed that the reduction in this case proceeds through the intermediate formation of tetraalkylammonium radicals adsorbed on the surface of the mercury cathode:



$$(Alk)_4N^+ \xrightarrow{e} [Alk_4N^0]_{ads}$$

$$4\,Alk_4N + ArC(=O)OR \xrightarrow[-H_2O]{4H^+} Alk_4N^+ + ArCH_3 + ROH$$

Mairanovskii [3] demonstrated the polarographic activity of benzoic-acid esters in dimethylformamide and expressed the hypothesis that the observed polarographic wave corresponds to the rupture of the C–O bond. It was reported in [4] that both esters of aromatic acids and esters of aliphatic acids with aromatic-alcohol residues are polarographically active in dimethylformamide solutions. In the latter case, the bond with the aromatic residue is ruptured and the free acid regenerated:



$$Alk\overset{O}{\underset{O-Ar}{C}} \xrightarrow{2H^+,\,2e} Alk\overset{O}{\underset{OH}{C}} + ArH.$$

There are no data in the literature concerning the electrolytic cleavage of the C–O bond in aliphatic esters. We have established that several aliphatic esters decolorize hexamethylphosphorotriamide solutions containing solvated electrons. The solvated electrons were obtained by electrochemical generation [5]. The experiments were performed with an H-shaped cell (Fig. 1). The cathode and anode compartments were separated by a stopcock with a large opening into which a glass filter was sealed. The catholyte and the stopcock were provided with a jacket for coolant water. The cathode compartment, with a copper electrode, was provided with a microburet for adding reducing agent. The cathode compartment and the microburet were purged with argon to remove oxygen. Since the supporting-electrolyte salt becomes depleted as electrolysis progresses, excess salt was added to the electrolyzer. To maintain a constant concentration of supporting electrolyte, the catholyte was mixed with a magnetic stirrer. The synthesis was carried out at a temperature of 10°C. A constant temperature was maintained by means of a U-3 universal thermostat. The current density was 0.2 A/cm^2. The reduction was carried out in two ways.

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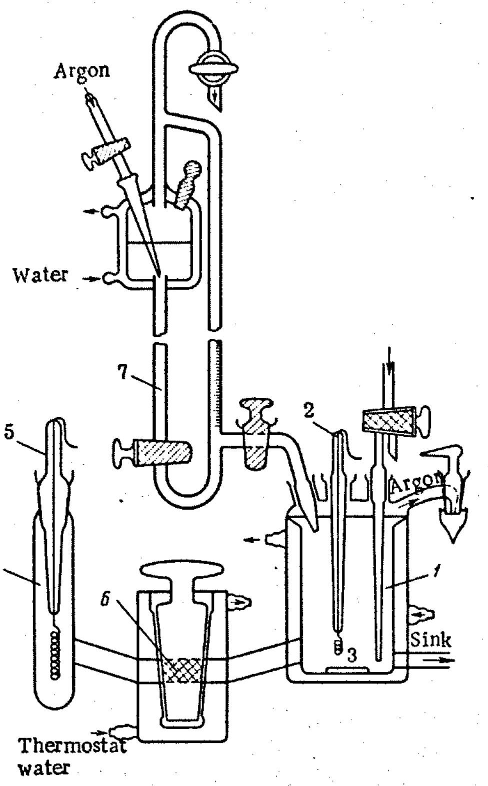
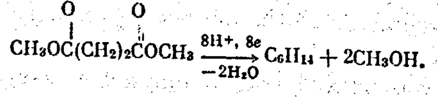


Fig. 1. Cell for preparative electrolysis: 1) cathode compartment; 2) cathode; 3) stirrer; 4) anode compartment; 5) anode; 6) stopcock with glass filter; 7) microburet.

The first way consisted in the following: The whole amount of reducing agent and proton donor was placed in the cathode compartment of the cell, after which electrolysis was effected. Reduction could take place both at the electrode and by reaction with solvated electrons.

The second way consisted in the following: Dimethyl adipate and a proton donor are added to a solution containing electrochemically-pregenerated solvated electrons by means of the microburet in an amount sufficient to leave a small excess of solvated electrons. A chemical reaction between the dimethyl adipate and the solvated electrons took place. Ethanol was used as the proton donor. The ethanol was added to the dimethyl adipate in a molar ratio of 2 : 1. After electrolysis, the solutions were analyzed by gas chromatography (stationary-phase polyethylene glycol 20,000 on zeolite; temperature 200°; flame-ionization detector; detector current 100 μA; detector temperature 200°; column length 2 m; evaporator temperature 320°). In the case of reduction by the first method, the initial mixture showed a pronounced peak corresponding to dimethyl adipate. As electrolysis progresses, this peak decreases in size and then disappears completely, which indicates that the dimethyl adipate has undergone reaction, while the chromatogram shows the presence of a low-boiling fraction which, in efflux time, corresponds to hexane. We can conclude that the reduction of dimethyl adipate proceeds with rupture of the C–O bond, as in the case of the esters of aromatic acids:



$$CH_3O\overset{\overset{O}{|}}{C}(CH_2)_2\overset{\overset{O}{\|}}{C}OCH_3 \xrightarrow[-2H_2O]{8H^+,\ 8e} C_6H_{14} + 2CH_3OH.$$

It was not possible to obtain α, ω-glycols by this method. Both methods of reduction gave the same product. This leads us to suppose that the reduction of dimethyl adipate proceeds by a chemical route in both cases, i.e., by reaction with solvated electrons. This is also indicated by the presence of a thin film with the blue color characteristic of solvated electrons at the cathode during electrolysis by the first method.

LITERATURE CITED

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