

COMPETITIVE REACTIONS METHOD IN ELECTROCHEMISTRY. A NEW TOOL FOR INVESTIGATING THE ANODIC INTERMEDIATES REACTIVITY

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Abstract—Some application features of the competitive reactions method (C.R.M.) for anodically generated agents have been considered. Quantitative characteristics of the $(RO)_3P$, $(RO)_2POSiMe_3$, $(EtO)_2PONa$, and I_2 electrochemically induced intermediates have been presented. It is discussed how to apply the obtained information for stating the nature of respective species.

INTRODUCTION

It is an urgent aim of organic electrochemistry to study the reactivity of electrochemically activated intermediates. A distinguishing feature of the most of these particles is a short life time which does not permit either to study the following chemical reactions using kinetic procedures or to state an existence of such an intermediate itself. Yet in a practice of organic chemistry the C.R.M. developed by Ingold during the investigation of electrophilic substitution reactions[1] is widely used. The method being based on the determination of the relative reactivity through analysis of the reaction products composition, it has a low sensitivity to by-processes. This is a valuable circumstance from the electrochemical point of view. For the first time the C.R.M. has been used for investigating electrochemically induced processes under studying the trialkylphosphite radical cations reactivity[2, 3]. The works using this approach for studying the reactivity of electrochemically produced dinitromethyl-radicals[4] and nitronium cations[5] have been published recently. This shows a fruitfulness of the electrochemical version of the C.R.M. The C.R.M. abilities to define the nature and reactivity of the anodic oxidation intermediates as well as comparing of experimental features of electrochemical C.R.M. version with non-electrochemical one will be considered in this paper.

EXPERIMENTAL

Electrochemical oxidation was carried out in the divided glass cell. The anode was a Pt-cylinder (unless otherwise specified) with a surface area of *ca* 50 cm². The cathode was a Ni-spiral. Dry MeCN was used as a solvent; sodium perchlorate as a supporting electrolyte. A potentiostat P-5827M was used as a source of a constant current. A reference electrode was Ag/0.01 M AgNO₃ in MeCN. In all runs a saturated solution of NaClO₄ in MeCN was a catholyte.

Anodic phosphorylation of aromatics

100 ml of the anolyte contained 0.06 mol of organophosphorus depolarizer and 0.06 mol of each of aromatics. On passing of 0.011F with a current density of 2 mA cm⁻² the anolyte was concentrated in vacuum, washed by water, extracted with ether, dried with MgSO₄, concentrated again and analysed by GLC.

Anodic iodination of aromatics

100 ml of the anolyte contained 0.2 mol of both aromatics and 0.04 mol of elemental iodine. 0.0075F was passed with the current density of 0.2 mA cm⁻². Then the anolyte was concentrated in vacuum. The residue was washed by aqueous Na₂SO₃ and Na₂S₂O₃ solution and extracted with ether. The extract was dried with MgSO₄, concentrated and analysed by GLC and ¹H NMR.

Synthesis of CH₃-C⁺=N-I

60 ml of the anolyte contained 0.028 mol of iodine. The electrolysis was carried out with the current density of 7 mA cm⁻². On passing of 0.65F under the anode potential of 1.7 V the anolyte was cooled to *ca* -25°C, filtered, quickly washed by cooled MeCN and dried in vacuum at a room temperature.

Photochemical phosphorylation

The solution of 0.15 mol of benzene and its derivative, 0.03 mol of diethylphosphite, and *t*-butylperoxide was placed into a reaction quartz vessel where it was irradiated by a DRS-250 *uv*-source stirring in Ar-atmosphere. Then the mixture was concentrated in vacuum and analysed by GLC.

GLC-analysis was carried out on a "Chrom-4" flame ionization instrument equipped with 220 × 0.3 cm glass columns (5% Silicone SE-30 on Chromaton N-AW (0.125-0.160 mm)). To separate the chlorophenylphosphonate isomers 15% polyethylene