React. Kinet. Catal. Lett., Vol. 34, No. 2, 383-388 (1987)

ELECTROCATALYTIC OXIDATION OF CYCLOHEXANE BY MOLECULAR OXYGEN IN THE PRESENCE OF TERTIARY ALKYLAMMONIUM SALTS IN NON-AQUEOUS SOLVENTS

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Received September 4, 1986
Accepted February 11, 1987

A new electrocatalytic system (acetonitrile, quaternary ammonium salt, graphite cathode) for oxidizing cyclohexane to cyclohexanol by molecular oxygen at room temperature has been discovered.

Обнаружена новая электрокаталитическая система (ацетонитрил, четвертичная аммониевая соль, графитовый катод), позволяющая окислять циклогексан в циклогексанол молекулярным водородом при комнатной температуре.

Oxygen reduction is known as one of the methods for its activation to oxidize organic compounds. Electrochemical reduction of oxygen in an aqueous solution of a phosphate buffer has been used previously [1-3] for the hydroxylation of aniline to p-aminophenol. Some attempts to oxidize alkanes in these systems failed. After going to non-aqueous solvents, several new systems were discovered for the selective oxidation of alkanes by reduced oxygen to either alcohols or ketones at room temperature. Here we present the results of studying the electrocatalytic oxidation of cyclohexane on a graphite cathode by molecular oxygen in a solution of acetonitrile in the presence of tetraalkylammonium salts.

Electrolysis was carried out in acetonitrile solutions containing various alkylammonium salts (tetraethylammonium (TEAB) and tetrapropylammonium (TPAB) bromides, tetrabutylammonium hydrosulfate (TBAHS)) as supporting electrolytes. All experiments were performed in a 11 cm^3 temperature-controlled three-electrode reaction cell with separated cathode (4-5 cm^3) and anode regions. The cathode was a 3.5 cm^2 graphite plate, the anode was glassy carbon and the reference electrode (RE) was acetonitrile-based $Ag/AcCl_{sat}$ + $LiCl_{sat}/LiCl$. All experiments were made at 293 K under continuous purging by oxygen. Cyclohexane concentration was 10 vol.%. Reaction products were analyzed by GLC method on a LKhM-8 chromatograph.

Acetonitrile was purified like in Ref. [5]. Tetraalkylammonium salts ("Serva" products) were dried in vacuum and used without additional purification. Cyclohexane was distilled before use.

Electrocatalytic oxidation was carried out at a constant cathode potential In various experiments it was ranging from -1.4 to -0.7 V (oxygen reduction starts at -0.65 V with respect to RE). Without oxygen the background current is not greater than 2 % O_2 current. The main product of cyclohexane oxidation is cyclohexanol. With deep oxidation degrees one can also observe the formation of cyclohexanone that is the product of electrolytic oxidation of cyclohexanol by molecular oxygen. Oxidation of 10^{-2} mol/dm^3 cyclohexanol in acetonitrile containing $2x10^{-2}$ mol/dm^3 TPAB for 50 min produces $4x10^{-3}$ mol/dm^3 cyclohexanone with about 1.8 % electrochemical yield.

Formation rate of cyclohexanol from cyclohexane and the electrochemical yield depend on both the concentration of tetraalkylammonium salts and the quantity of electric current passed through the solution (Fig. 1). With a certain concentration of the salt the formation rate of alcohol increases with growing quantity of electricity passed through the solution or, in other words, with rising time of electrolysis. With increasing initial concentration of the salt, the formation rate of cyclohexanol decreases. The plotted dependences in Fig. 1 can be treated if one suggests that tetraalkylammonium salts

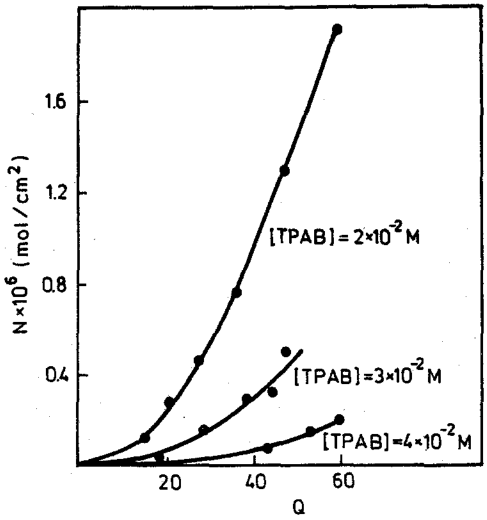

Fig. 1. Dependence of the number of cyclohexanol moles formed by electrocatalytic oxidation of cyclohexane, on the amount of electric current passed through solution at various concentrations of tetrapropylammonium bromide

are the competing substrates for cyclohexane oxidation by reduced oxygen. This suggestion seems to be reasonable, since the oxidation of alkyl groups of tertiary ammonium salts can follow the same mechanism as that of cyclohexane. Besides, the participation of tetraalkylammonium salts in reactions with reduced oxygen was observed in experiments. Thus, during the electrochemical reduction of oxygen in DMSO solutions in the presence of tetraethylammonium perchlorate [6] the formation of triethylamine, ethylene and dimethyl sulfate was observed. The authors of Ref. [6] believe that hydrogen detachment from the ethyl radical takes place under oxygen reduction by a second electron

$$O_2^- + e^- + (C_2H_5)_4N^+ \longrightarrow HO_2^- + C_2H_4 + (C_2H_5)_3N$$

$$HO_2^- + (CH_3)_2SO \longrightarrow OH^- + (CH_3)_2SO_2$$

and the HO_2^- formed oxidized DMSO to dimethyl sulfate. It is possible that with a significant difference in the TPAB and cyclohexane concentrations ($2x10^{-2}$ mol/dm^3 and 1 mol/dm^3, respectively), the proton required for O_2 reduction by a second electron is also detached from cyclohexane

$$C_6H_{12} + O_2^- + e^- \xrightarrow{\text{electrode}} C_6H_{11}^- + HO_2^-$$

Further oxidation of a carbanion by molecular oxygen produces an alcohol. The detailed oxidation mechanism of both tetraalkylammonium salts and cyclohexane by reduced oxygen, however, has not been studied. At present we can only say that the behavior of the salts does not depend on the length of alkyl radicals over the range from 2 to 4 carbon atosm (Fig. 2).

It is known that the products of one-electron reduction of oxygen, i.e. O_2^-/HO_2 radicals do not oxidize alkanes at room temperature in a liquid phase [7]. The addition of hydrogen peroxide to the solution in the quantities that would be able to form during electrolysis, did not produce cyclohexanol for the same time period.

Electrochemical reduction of tetraalkylammonium salts produces alkyl radicals [8]. If one suggests that small quantities of radicals can be formed before achieving the potentials of salt reduction; these radicals could have initiated the chain oxidation of cyclohexane by oxygen. It has been established, however, that the formation rate of cyclohexanol is independent of the cathode potential (Fig. 2). Apparently, the contribution of a chain reaction is not decisive.

Therefore, it can be suggested that the oxidation of cyclohexane by reduced oxygen does take place on a graphite electrode

$$C_6H_{12} + O_2 \xrightarrow[R_4N^+]{\text{graphite, } e^-} C_6H_{11}\,OH \qquad (1)$$

The maximum electrochemical yield in reaction 1 with TPAB =

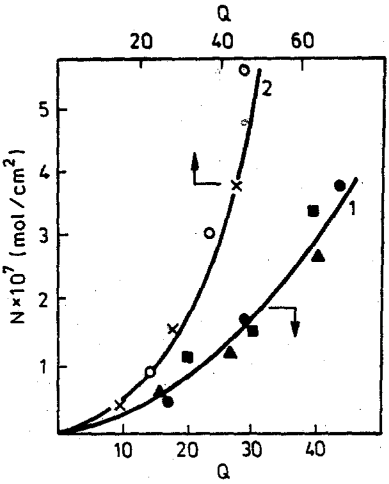

Fig. 2. Influence of the alkyl group length of the quaternary ammonium salt (curve 1) and of cathode potential (curve 2) on cyclohexanol yield
▲ - [TEAB] = 3×10^{-2} mol/dm^3; ● - [TPAB] = = 3×10^{-2} mol/dm^3; ■ - [TBAGS] = 3×10^{-2} mol/dm^3;
o - ϕ = -1.4 V, x-ϕ= -0.8 V

= 2×10^{-2} mol/dm^3 per two-electron reduction of oxygen is equal to 1.6 %. This low values are, apparently, due to the competition of tetraalkylammonium salts. The overall concentration of cyclohexane oxidation products for 90 min electrolysis (60 coul.) is 1.1×10^{-3} mol/dm^3 at the initial concentration of about 1 mol/dm^3. Without oxygen no products of cyclohexane oxidation are formed.

Reaction 1 can also take place on a cathode made of glassy carbon, but under the same conditions the yield of cyclohexanol is an order in magnitude lower. Apparently, it is due to the less effective surface area of glassy carbon compared to graphite.

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