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ELECTROCATALYTIC REDUCTION OF POLYHYDRIC

ALCOHOLS TO HYDROCARBONS

G. N. Petrova and O. N. Efimov

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A study was carried out on the electrochemical reduction of polyhydric alcohols using an iron-coated titanium cathode. The mechanism of this reaction was discussed.

There is no information in the literature on the electrochemical reduction of polyhydric alcohols to hydrocarbons. In a previous work [1], we noted the high reactivity of Ti(0) in the reduction of carbonyl compounds and polyhydric alcohols to olefins. The formation of pinacol derivative (III) coordinated with titanium was proposed as the intermediate.

$$\begin{array}{c} 1 \\ 1 \\ (I) \\ (II) \\ (II) \\ (III) \\ (IIII) \\ (III) \\ (III) \\ (III) \\ (III) \\ (III) \\ ($$

The reduction of a dihydric alcohol is possible only upon the simultaneous coordination of two adjacent oxygen atoms to two Ti(0) atoms [1]. Dry organic solvents were used for these reactions. We attempted to carry out these reactions electrochemically. However, it is difficult to obtain an oxide-free titanium cathode surface.

In previous works [2,3], we showed that the introduction of iron and manganese into an aluminum cathode facilitates catalysis of the electrochemical reduction of CO in weakly acidic aqueous solutions with the formation of C_1-C_3 hydrocarbons. In alkaline solutions, in which aluminum readily dissolves, these metals may be used as a catalyst upon deposition on the surface of a titanium electrode by the chemical (NaBH₄) or electrochemical reduction of solutions of the corresponding salts or thermal decomposition of their carbonyls. The oxide film formed on titanium does not hinder the electrochemical reaction. Under the conditions for the reduction of CO on the modified electrodes, formaldehyde and methanol are not reduced and, thus, the reduction of CO to hydrocarbons proceeds without the formation of intermediates and their entry into the solution. Since the formation of C_2-C_3 hydrocarbons requires dimerization of C_1 -intermediates, we may assume that the electrochemical reduction of CO proceeds similarly to the scheme for diols and, thus, we may expect the reduction of polyhydric alcohols capable of forming intermediate (III). The difference lies in the circumstance that the function of Ti(O) is carried out by Fe(O) or Mn(O) atoms,

Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1697-1699, July, 1991. Original article submitted January 4, 1991. which may be reduced electrochemically to the initial state in aqueous media after formation of oxide derivatives. This provides a catalytic variant of the reaction.

EXPERIMENTAL

The reduction was carried out in a potentiostatic mode using a P-5827 potentiostat in an electrochemical diaphragm cell. The anodic and cathodic spaces were separated by a glass frit [4]. The potentials are given relative to the saturated calomel electrode. The cathode was an iron-coated titanium disk with 30 mm diameter. Aqueous 0.1 N NaOH was used as the electrolyte. The solution was stirred with a magnetic stirrer and the circulating gas mixture. The hydrocarbon content was determined by gas chromatography.

RESULTS AND DISCUSSION

A (4-6):1 mixture of propylene and propane was observed in the gas phase upon the electrochemical reduction of glycerin. Propyl alcohol was not observed as a possible product of the reduction of glycerin and this alcohol is not reduced under these conditions. Hydrocarbon formation from glycerin is observed at potentials below -1.4 V and the reaction rate is independent of the potential in the range from -1.6 to -1.9 V. The reaction stops when the current is turned off. Thus, this is indeed an electrochemical reaction. The electron transfer step is not rate-limiting.

The rate of glycerin reduction depends on the concentration of alkali in the solution and decreases by a factor of 2.5 with an increase in the alkali concentration from 0.05 to 5 moles/liter.

It is interesting to note that the presence of O_2 affects neither the reaction rate nor product ratio and, thus, there cannot be free-radical intermediates. Most likely, the intermediates are strongly bound to the surface, as indicated by the lack of propyl alcohol in the solution. The current yield is ≤ 0.1 % due to the significant liberation of H₂. For this reason, the reaction rate is reduced by a factor of 4-5 upon replacing the titanium cathode with a platinum cathode. However, the current yields on vitreous carbon and lead electrodes with higher hydrogen overpotential are comparable with those on the titanium cathode since hydrogen is released mainly on supported iron on these three electrodes.

The products of the electrochemical reduction of ethyleneglycol are methane, ethylene, and ethane in 1:2:2 ratio. This corresponds to the conversion of pinacol derivative (III) into (II), i.e., cleavage of a C-C bond with subsequent reduction of (II) to methane. Of course, such a reaction is possible only in protic media, in which the M-C bond may be cleaved protolytically. The lack of cleavage products in the case of glycerin may be related to stabilization of allyl complexes on the electrode surface, which cannot exist in the case of ethyleneglycol.

The most convincing evidence for an electrochemical course for the reduction of polyhydric alcohols according to the proposed scheme, in our view, may lie in the difference in the reactivities of 1,2- and 1,3-propyleneglycols. In complete accord with this scheme, 1,2-proplyleneglycol is reduced to propylene and propane in 10:1 ratio, while the rate of the reduction of 1,3-propyleneglycol containing separated hydroxyl groups is very low and leads to trace amounts of hydrocarbon.

Tetramethylethylene is not formed in the electrochemical reduction of acetone. Only propane and propylene (in 3:1 ratio) are found in the gas phase. This result may also be related to the formation of strong surface allyl iron complexes incapable of dimerizing.

Despite the low current yields of the products, the electrochemical reduction of carbonyl compounds and polyhydric alcohols hold undoubted interest since they are similar to the chemical reduction of these substrates on metal surfaces. The ratio between the hydrogen liberation from water and the reduction of the substrates may depend strongly on the size of the catalyst particles, their localization on the surface, and a series of other factors, which may be controlled by developing more complex, chemically modified electrodes.

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SYNTHESIS OF STERICALLY HINDERED AROMATIC DIALDEHYDES

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A. P. Yakubov, D. V. Tsyganov, L. I. Belen'kii, and M. M. Krayushkin

A study was carried out on the formylation of a series of aromatic compounds containing two mesitylene or durene residues [dimesityl (I), dimesitylmethane (II), 1,2-dimesitylethane (III), 1,6-dimesitylhexane (IV), dimesityl sulfide (V), 1,1-dimesitylethylene (VI), 1,1-dimesityl-1-butene (VII), and didurylmethane (VIII)] by the action of dichloromethyl methyl ether (DCM) in the presence of AlCl₃ and TiCl₄. The corresponding dialdehydes are the major products. The formylation products when the reaction is carried out in the presence of AlCl₃ in the case of (I) and (V) contain significant amounts of monoaldehydes, while partial cleavage of the substrates with the formation of products containing only one benzene ring is observed in the case of (II) and (VIII) in addition to formylation.

In a previous work [1], we proposed a modified procedure for Rieche formylation by the action of dichloromethyl methyl ether (DCM), which permits the smooth conversion of mesitylene to the corresponding aldehyde in high yield. This procedure also permitted discovery of a previously unknown reaction course, leading not to aldehydes but rather to the corresponding dichloromethyl derivatives. This reaction course is especially evident upon carrying out the reaction in the presence of aluminum chloride. Cleavage of the substrate is also observed in the case of the formylation of dimesitylmethane with the formation of products with only one benzene ring [1].

In the present work, we studied the effect of the nature of the condensing agent $(AlCl_3 \text{ or } TiCl_4)$ on the reaction course and optimized the synthesis of dialdehyde from a series of available compounds containing two mesitylene or durene residues. Such dialdehydes hold interest for further transformations, in particular, to new stable bisnitrile oxides.

The starting compounds were dimesityl (I), dimesitylmethane (II), 1,2-dimesitylethane (III), 1,6-dimesitylhexane (IV), dimesityl sulfide (V), 1,1-dimesitylethylene (VI), 1,1-dimesityl-1-butene (VII), and didurylmethane (VIII).



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1700-1703, July, 1991. Original article submitted January 28, 1991.