TELOMERIZATION OF ETHYLENE BY ANODICALLY GENERATED CHLORINE

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Reactions of addition of anodically generated chlorine to olefins have attracted the attention of investigators for a long time. Processes of the electrochemical chlorination [1] and chlorohydroxylation [2, 3] of ethylene in an aqueous medium and also chloroalkoxylation in anhydrous methanol [4] have been studied in greatest detail.

The purpose of the present paper is elucidation of the basis possibility of electrochemical telomerization of ethylene by anodically generated chlorine radicals because higher dichloroalkanes are of considerable practical interest as intermediates for industrial synthesis of high-molecular-weight compounds.

We determined that 1,2-dichlorethane, 1,4-dichlorbutane (in yields up to 10%), and bis(2-chloroethyl) ether were formed during electrolysis of hydrogen chloride in methanol or aqueous acetonitrile ($H_2O:MeCN=1:8$)* at a platinum anode (current density of 50 A/m²) in the presence of ethylene under pressure up to 6.5 MPa, and we also determined that 1-methoxy-2-chloroethane was also formed in methanol.

The formation of these products can be represented as follows:

Scheme

$$ClCH_{2}CH_{2}OR \quad (R = H, CH_{3})$$

$$ROH/-H^{+} \uparrow (7)$$

$$Cl_{2} \xrightarrow{C_{2}H_{4}} ClCH_{2}CH_{2}Cl \leftarrow \xrightarrow{Cl^{-}} ClCH_{2}CH_{2}CH_{2}+ \xrightarrow{ClCH_{3}CH_{2}OH^{-}/-H^{+}} ClCH_{2}CH_$$

The atomic chlorine that is formed in electrochemical oxidation of the chloride anion at the anode can either undergo dimerization with the formation of molecular chlorine or undergo addition at the double bond with the formation of $ClCH_2CH_2$ radicals (I) in the presence of an adsorbed acceptor [5]. These intermediate species are similar in nature to those that appear during electrochemical oxidation of 3-chloropropionic acid and, as is known, can recombine, giving 1,4-dichlorobutane [6]. The formation of this product is also possible because of reactions (9) and (12) (see the scheme). However, as we showed previously [7], 1,4-dichlorobutane appears mainly because of recombination of radicals (I).

The key steps in the investigated process are probably the steps of generation of radicals (I) and their oxidation to carbonium ions $ClCH_2C\dot{H_2}$, which react easily with nucleophilic reagents present in solution [8]. The possibility of the formation of carbonium ions from radicals (I), whose ionization potential exceeds 8 eV, has not been refuted in the literature [9].

The formation of 1-methoxy-2-chloroethane (47%) and bis (2-chloroethyl) ether (17%) during electrolysis of a methanol solution and bis (2-chloroethyl) ether (11%) during electrolysis of a water-acetonitrile solution due to recombination of generated methoxy (CH₃O) and chloropropionyl (Cl CH₂CH₂CO) radicals with radicals (I) seems unlikely because alkoxy radicals are generated [10] only in highly alkaline media during electrochemical oxidation of alkanols. In considering the contribution of reactions of chemical chlorination of ethylene in solu-

*Significant resinification was observed in anhydrous acetonitrile because of polymerization of the acetonitrile.

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tion (reaction (11) to the overall process, it is important to note that the rate of chemical chlorination should not depend on the electrode potential.

The kinetics of processes of formation of 1,2-dichloroethane and 1,4-dichlorobutane according to a radical mechanism can be described by equations taking into account the adsorption of the acceptor on the uniformly inhomogeneous surface of platinum [11]

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$$v_2 = k_2 i \theta_1 \exp (\beta f \theta_1)$$

$$v_3 = k_3 i v_2 = k_3 i^2 \theta_1 \exp (\beta f \theta_1)$$

$$v_4 = k_4' v_2 = k_4 i^2 \theta_1^2 \exp (\beta f \theta_1)$$

where k_2 , k_3 , and k_4 ' are rate constants of the formation of radicals (I), 1,2-dichloroethane, and 1,4-dichlorobutane, respectively; θ_1 is the filling of the surface with ethylene; i is the current density, A/m^2 ; β is the migration coefficient; and f is the surface-inhomogeneity factor. The rate of the competing reaction of formation of molecular chlorine is

$$v_{10} = k_{10} \, [\text{Cl}]^2 = k_{10} i^2$$

It should be expected that with decreasing current density the rate of the competing reaction of formation of molecular chlorine would decrease because this reaction has a second order with respect to radicals, and it should be expected that the ratio of the rates of formation of 1,4-dichlorobutane and 1,2-dichloroethane would increase because this quantity is proportional to the filling of the surface with ethylene.

$$v_4/v_3 = k\theta_1$$

Change of the current density and, therefore, the potential of the platinum anode in a wide range had practically no effect on the change of the ratio of the yields of 1,4-dichlorobutane and 1,2-dichloroethane, apparently because of the weak dependence of the ethylene filling of the electrode surface on the potential and strong competition of the chloride anions and ethylene during their adsorption.

Therefore, the formation of 1,2-dichloroethane was probably determined by chemical chlorination (Eq. (11)) in solution and by chlorination proceeding via the carbonium ion (6), and the yield of 1,4-dichlorobutane depended on the reactivity of intermediately appearing radicals (I) and the ethylene concentration on the surface of the platinum anode.

Thus, in parallel with the telomerization of ethylene by anodically generated chlorine radicals, competing processes of chemical chlorination and oxidation of secondary radicals to carbonium ions occurred, leading to the formation of products of nucleophilic addition.

EXPERIMENTAL

Preparative electrochemical synthesis was carried out in a high-pressure diaphragmless stainless-steel electrolyzer with platinum electrodes. Methanol or a water-acetonitrile solution saturated with hydrogen chloride was poured into a 100-ml Teflon beaker, and ethylene was fed into the electrolyzer under pressure. The electrolyte was stirred with a magnetic stirring device. The electrolyzer was placed in a vessel with a mixture of dry ice and acetone, keeping the temperature at 5-10°C. After completion of electrolysis, the reaction mixture was diluted with water saturated with CaCl₂, and it was extracted with ether. The ether extract was washed with a 5% solution of NaHCO₃ and with water, was dried over anhydrous MgSo₄, and ether was distilled off. The residue was distilled in vacuo and analyzed on a LKhM-8MD chromatograph (FS-1265 stationary phase, 145°C) and Varian CH-8 chromatograph-mass spectrometer (FS-1265 stationary phase), with an initial temperature of 50°C and programmed heating from the 10th minute at a rate of 6 deg/min to 180°C.

Electrolysis of Hydrogen Chloride in the Presence of Ethylene in MeOH. Into an electrolyzer was placed 50 ml of MeOH saturated with hydrogen chloride (3.5 g), with an ethylene pressure of 6.0 MPa and current density of 200 A/m², and 5 A-h of current was applied. Isolated: 2.1 g of a liquid containing (according to GLC data) 31 % ClCH₂CH₂Cl mass spectrum: 98 (M⁺); 47% CH₃OCH₂CH₂Cl according to GLC agrees with the definitely pure compound synthesized according to [4]; 6% ClCH₂CH₂CH₂CH₂Cl mass spectrum: 90 (M⁻ HCl); 17% ClCH₂ · CH₂OCH₂CH₂Cl mass spectrum 142 (M⁺). The mass spectra of the 1,2-dichloroethane, bis (2-chloroethyl) ether, and 1,4-dichlorobutane obtained in this experiment run and also in the experiment run described below agreed with the spectra of these compounds given in [12].

Electrolysis of Hydrogen Chloride in the Presence of Ethylene in MeCN:H₂O=8:1. Into an electrolyzer was placed 50 ml of a mixture of MeCN and H₂O (8:1) saturated with HCl (3.5 g), ethylene was added (pressure of 6.0 MPa), with a current density of 200 A/m², and 12 A-h of current was applied. Isolated 2 g of a liquid containing (according to GLC data) 82% ClCH₂CH₂Cl, 6% ClCH₂CH₂CH₂CH₂Cl, and 11% ClCH₂CH₂OCH₂CH₂Cl.

CONCLUSIONS

1,2-Dichloroethane, 1,4-dichlorobutane, and bis (2-chloroethyl) ether were obtained by the reaction of ethylene and anodically generated chlorine radicals in methanol and in aqueous acetonitrile, and 1-methoxy-2-chloroethane was also obtained in methanol.

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SYNTHESIS OF UNSATURATED ALCOHOLS

BY TELOMERIZATION OF H₂O WITH 1,3-DIENES,

CATALYZED BY PALLADIUM COMPLEXES

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The activation of H_2O molecules in their reaction with butadiene by means of low-valent phosphine complexes of palladium has provided the basis for a promising method for the preparation of 1,7- and 2,7-octadienols (I) and (II) [1-7]. It has been shown to be possible to prepare nonadienols by the concurrent telomerization of butadiene and isoprene with H_2O [8]. A necessary condition for the successful accomplishment of these reactions is the inclusion of CO_2 in the composition of the catalyst. The relatively high consumption of catalyst and the low selectivity of these reactions [1-8] renders them of little use for the preparation of unsaturated alcohols.

In order to develop a selective method for the synthesis of octadienols, and for the preparation of other unsaturated alcohols, the reaction of 1,3-dienes with complexed H_2O , catalyzed by palladium compounds, was first examined. It would be expected that H_2O present in crystalline hydrates of the type $MX_n(H_2O)_m$ would be activated by complexation with the central metal atom, and would react with 1,3-dienes more readily than free H_2O to give alcohols (I) and (II). Preliminary experiments showed that butadiene reacted with complexed H_2O over the catalyst $Pd(acac)_2 - PPh_3 - AlEt_3$ in the absence of CO_2 .

Thus, telomerization of butadiene with the complex $CuSO_4 \cdot 5H_2O$ in the presence of this catalyst (Pd : PPh₃:Al=1:3:4, 90°C, 6 h) in acetone gave a mixture of unsaturated alcohols consisting of (I), (II), and the ether (III) in an overall yield of ~50%, calculated on H₂O. The yields and compositions of the telomerization products varied considerably depending on the reaction conditions and the diene :H₂O ratio

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