Electrochemical hydrogenation of citral 3.* Effect of the nature of the solvent on electrocatalytic hydrogenation at a copper cathode

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The effect of a water-organic mixed solvent of varying composition $(H_2O-DMF, H_2O-EtOH)$ on the selectivity of electrocatalytic hydrogenation of citral at a copper cathode was studied. The experimental results were discussed from the standpoint of the effect of the solvent structure on the heterogeneous electrochemical process involving a bulky organic molecule.

Key words: citral, electrocatalytic hydrogenation; copper cathode; solvent structure.

It is known that the nature of the solvent is one of the main factors determining the mechanism and direction of an electrochemical process.¹ A distinguishing feature of electrocatalytic hydrogenation (ECH) is that it is accomplished by electrochemically generated hydrogen. Therefore, in this process, one should use solvents with high dielectric constants containing proton donors, in particular, water or water-organic mixtures. Many regularities of the effect of solvents on the rates and mechanisms of chemical reactions occurring in the bulk of a solution are known.² It has also been shown that the selectivity of catalytic hydrogenation of citral depends on the nature of the solvent,³ however, no systematic data dealing with the effect of the solvent on ECH have been published. Nevertheless, it is known than the ECH process is hampered when a bulky organic molecule acts as the substrate. In fact, ECH of pseudoionone⁴ in aqueous ethanol or aqueous dioxane was carried out only with intense stirring (up to 1000 r.p.m.).

In the previous paper⁵ we have shown that the selectivity of the ECH of citral at a copper cathode varies substantially with the proportion of DMF in H_2O . The present study is devoted to a more detailed consideration of the effect of the nature of the solvent on the ECH of citral.

Experimental

The experimental equipment and the procedures for the electrolysis and quantitative analysis of the products were described in our previous paper.⁵

Electrolysis was carried out at a copper cathode, preliminarily annealed in the flame of a glass-blowing burner and

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treated with dilute HNO₃ (1 : 10); a saturated calomel electrode was used as the reference electrode, and H_2O —EtOH and H_2O —DMF mixtures with varying compositions were used as solvents. The ratio between the concentrations of citral and acetic acid was 1 : 10 (mol/mol). The ratio between the yields of isomeric nerol and geraniol in all runs corresponded to the ratio between the concentrations of neral and geranial in the starting citral, as shown by GLC and ¹H NMR spectroscopy.

Results and Discussion

It has been shown previously⁶ that ECH of citral at a copper cathode in the presence of AcOH yields alcohols, namely, citronellol (1) and isomeric nerol and geraniol (2), as the major products. In some cases, formation of some citronellal (3) has also been detected.



When an H_2O-DMF (60 : 40) mixture is used as the solvent and a tenfold excess of AcOH with respect to

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citral is taken, the overall yield of alcohols 1 and 2 is ~ 90 %, and the 1 : 2 ratio reaches 4.8. It has been of interest to study the possibility of conducting ECH of citral in the solvents that are most frequently used in electrosynthesis, namely, alcohols and aqueous alcohols.

The presence of methanol chemisorbed on a Pt electrode is known⁷ to change the selectivity of ECH of allyl alcohol. According to our data,⁶ storage of the copper cathode in hot MeOH prior to ECH of citral leads to a change in the product composition, viz., the ratio between the yields of alcohols dramatically decreases. We found that when the ECH of citral is carried out in H₂O-EtOH mixtures containing <30 % EtOH, alcohols 1 and 2 are formed in approximately equal amounts (Fig. 1), their overall yield being no more than 50 %. Hydrogenation occurs at the potential corresponding to the potential of hydrogen evolution (E =-1.2 V) and is accompanied by some resin-formation. When the concentration of EtOH in the solvent increases to >30 %, the yield of 1 and 2 decreases, and a substantial quantity of the substrate is recovered, although the amount of electricity passed through the solution (Q) is twice as high as that necessary for complete hydrogenation of citral ($Q_{calc} = 0.128$ A h). The proportion of oligomeric products also increases. In fact, in 50 % EtOH, the overall yield of alcohols 1 and 2 is ~ 30 % and the proportion of recovered citral is ~25 % (Q = 0.544 A h). When electrolysis is carried out in 70 % EtOH, only traces of alcohols and 70 % of the starting substrate are detected in the products, although evolution of hydrogen at E = -1.2 V takes place, and Q amounts to 0.260 A h. A similar situation is also observed when the solvent contains 90 % EtOH. In anhydrous EtOH, hydrogen is not evolved up to E = -1.9 V. At higher potentials, direct reduction of citral occurs.⁵

The ECH reaction is known⁷ to proceed on the electrode surface between a molecule of an organic



Fig. 1. Dependence of the yields of the products of ECH of citral on the proportion of EtOH in the solvent: 1, citronellol (1); 2, isomeric nerol and geraniol (2) (overall yield); 3, citronellal (3).

substrate activated due to the adsorption and adsorbed hydrogen atoms. Therefore, conditions that promote adsorption of citral would also be favorable for ECH. Adsorption of an organic substrate on an electrode, in its turn, depends on the solubility of the organic compound and also on the interaction of the solvent and/or the substrate with the electrode. Hence, the nature of the solvent and its properties exert appreciable effect on the course of the heterogeneous reaction.

The solubility of an organic compound in EtOH is higher than that in water or aqueous alcohols, and this deteriorates its adsorption.⁸ In fact, the surface concentration of an organic substrate, for example, in anhydrous MeOH is much lower than in aqueous MeOH.⁹ However, the fact that no products (alcohols 1 and 2) are formed when ECH is carried out in mixtures containing >70 % EtOH cannot be explained by merely the high solubility of the starting aldehyde. In fact, when anhydrous DMF, in which citral is more soluble than in alcohols, is used as the solvent, ECH occurs, though its selectivity is extremely low.⁵ Another reason for the retardation of ECH is probably the rather strong interaction of polar EtOH molecules with the negatively charged electrode.

The low yield of alcohols 1 and 2 as well as the nonlinear character of the dependence of the yields of ECH products on the EtOH proportion in the solvent can be understood by considering the properties of the solvents themselves and of their mixtures. It has been shown previously¹⁰ that as the composition of an H₂O-EtOH mixture gradually varies, its physicochemical properties vary non-monotonically; in particular, the viscosity of a 40 % solution of EtOH is almost three times higher than the viscosity of either of the components. In addition, water and ethanol are known to be structurized liquids. For example, high degree of association is inherent in EtOH, its molecules are bound via hydrogen bonds into long chain associates (up to 50 EtOH molecules, the coordination number is ~ 2), the concentration of free alcohol molecules being no more than 1 % (see Ref. 11). It may be assumed that the positively charged ends of these associates are arranged near the surface of the negatively charged electrode; thus blocking the electrode, they not only prevent adsorption of citral, but also retard the evolution of hydrogen. Therefore, the hydrogen evolution potential shifts somewhat to the negative side as the proportion of EtOH in the mixture increases.

The structure of a solution containing >0.5 mole fractions of EtOH (>70 %, v/v) mostly corresponds to the structure of pure alcohol,¹² and H₂O molecules are apparently easily incorporated into it causing no noticeable disturbances. This is in agreement with the smooth character of viscosity isotherms and isotherms of solubility of poorly soluble compounds.¹³ As the proportion of water in the mixture increases, the structure of the ethanol is gradually destroyed, and mixed associates of various compositions are formed.¹² In our opinion, it is

due to this process that at an EtOH concentration of <70 % the possibility of citral adsorption on the electrode and the possibility of ECH arise.

Water, in its turn, has an ice-like structure at ~20 °C, in which each molecule is surrounded by four other molecules located in the vertices of a tetrahedron due to formation of hydrogen bonds.¹⁴ The quasi-crystalline structure of water is also retained when up to 0.1-0.12 mole fractions of EtOH is added¹³ (which corresponds to ~ 20 %, v/v). Moreover, the structure of water is stabilized by the nonelectrolyte added.¹⁵ When ECH is carried out in an aqueous solution, the low solubility of citral should seemingly be favorable for its adsorption on the electrode surface, but the structure of the aqueous layer near the negatively charged surface prevents effective adsorption of the bulky organic molecule. The presence of up to 20-25 % (v/v) EtOH does not result in an increase in the yield of ECH products. which can be explained by the manifestation of the effect of stabilization of water structure.

When the proportion of ethanol in the mixture increases further, sharp transition to a different structural type followed by its gradual deformation occurs,¹³ *i.e.*, the structure of water is destroyed and mixed waterethanol linear associates are formed.¹⁵ This process is accompanied by an appreciable increase in the viscosity of the solution, whose maximum is achieved at an EtOH concentration of 0.25 mole fractions (~40 %, v/v), which corresponds to a EtOH : H₂O stoichiometric ratio of 1 : 3. Judging by the variation of the yields of ECH products, the electrochemical process is obviously decelerated, on the one hand, probably, due to the decrease in the rate of diffusion of the depolarizer to the electrode and the rate of removal of the reaction products, and on the other hand, due to the deterioration of the adsorption conditions.

It is noteworthy that the variations of diffusion coefficients of organic compounds as functions of the composition of a mixed solvent have previously been explained¹⁶ by variation of the degrees of association in these solutions. In particular, the viscosimetric and spectroscopic data obtained for $H_2O-MeOH$ mixtures indicates that in the region of the maximum viscosity of mixed solutions, $MeOH \cdot 3H_2O$ hydrates are formed. The authors cited believe¹⁶ that the formation of associates of this sort competes with solvation of the substrate molecules and thus affects the diffusion of molecules in the mixed solvent.

Thus, the variation of the product yields in the ECH of citral in aqueous ethanol correlates with structural rearrangements in the mixed solvent and indicates that the character of citral adsorption on the electrode varies as a function of the solvent composition.

In our previous paper⁵ we considered the effect of the composition of a H₂O-DMF mixture on the yields of the products of ECH of citral and showed that the plot of the product yields vs. the composition of the solvent has a parabolic form, the maxima of the yields of both alcohols being located at 40 % DMF in the solvent (Table 1, run 1). However, even small amounts of alcohols (5-10 %) added to this solution dramatically decrease the yield of compound 1 and the selectivity of ECH (see Table 1, runs 2 and 3), apparently, due to substantial deterioration of the adsorption conditions. It is also noteworthy that the results of electrolyses carried out in mixed solvents, whose composition corresponds to the maximum viscosity, are obviously similar to one another (see Table 1, runs 4-6). In these cases, in spite of prolonged electrolysis (5-6 h) and the knowingly excessive amount of electricity passed through the solution ($Q \approx 0.3$ to 0.4 A h), a considerable proportion of starting citral remains in the electrolysis solution, and the process is not selective and is accompanied by noticeable resin-formation. In the H₂O-EtOH system (see Fig. 1; Table 1, run 5), like the H₂O-DMF system⁵ (see Table 1, run 4), the highest yield of the side product, aldehyde 3, is obtained under the conditions of the maximum viscosity. The addition of 10 % DMF to aqueous ethanol having the maximum viscosity (run \mathcal{D}). does not lead to any substantial variations of the ECH process. The maximum viscosity of H₂O-DMF solutions is known to be attained at a DMF concentration of

Table 1. Yields of products of ECH of citral, *viz.*, citronellol (1), nerol and geraniol (2), and citronellal (3), as functions of the composition of the solvent ([Citral] = 0.024 mol L⁻¹, [AcOH] = 0.25 mol L⁻¹)

Run	Organic phase	Content of the starting		Yields of products (%)		
	(%, v/v)	sub	strate (%)	1	2	3
1	DMF (40 %)		_	74	16	
2	DMF (40 %) + MeOH (5	%)		35	23	10
3	DMF (40 %) + EtOH (10	%)*		38	19	
4	DMF (75 %)*		13	9	13	28
5	EtOH (40 %)		15	6	39	14
6	Pr ⁱ OH (50 %)*		23		15	2
7	EtOH (40 %) + DMF (10	%)	33		28	14

* [AcOH] = 0.5 mol L^{-1} .

~0.33 mole fractions (~70 %, v/v), which has been attributed¹⁷ to the formation of 2DMF \cdot H₂O mixed associates. Interaction of associates of this type with a negatively charged electrode should apparently be stronger than that of an organic molecule, and the mobility of these associates near the electrode is lowered, which may finally result in a retardation of citral adsorption and a decrease in the rate of hydrogenation.

It has been shown previously⁶ that further hydrogenation of aldehyde 3 (the product of 1,4-addition of an H atom to citral followed by rearrangement) gives citronellol 1 by a mechanism of hydrogen 1,2-addition. Therefore, it may be assumed that additional retardation of adsorption in the second step of hydrogenation under conditions of maximum solvent viscosity leads to the appearance of a considerable amount of aldehyde 3 in the product mixture and to a sharp decrease in the content of alcohol 1 or its complete absence (see Table 1, runs 4-7).

Our results imply that there is little point in using aqueous alcohols as solvents in the ECH of citral at a copper cathode (*i.e.*, in a heterogeneous electrochemical process involving a bulky organic molecule and occurring at a cathode with weak catalytic activity).

The regularities found for the variation of the yields of the products of ECH of citral as functions of the variation of the structure of solutions in H₂O-EtOH and H₂O-DMF mixtures allowed us to suggest that the previously described¹⁷ stabilization of the structure of water by small amounts of DMF added (~0.05 mole fractions, i.e., 17.5 % (v/v) DMF) may have an effect on the yields of products of the ECH of citral. Conducting a series of electrolyses in solvents, in which the DMF proportion varied from 0 to 25 %, showed that the curve of the dependence of the yield of compounds 1 and 2 on the concentration of DMF really exhibits a noticeable inflection in this region (Fig. 2), which is probably due to structural features of the solvent. This result provides further evidence in support of the effect of the structure of the solution on the results of ECH.

It should be noted that concentrations of the supporting electrolyte (0.1 M solution of KCl), citral $(0.024 \text{ mol } L^{-1})$, and acetic acid (up to 0.5 mol $L^{-1})$, used in the electrochemical process, are lower than those, which could cause a substantial variation of the structure of the solvent as a whole. In the case of the largest excess of AcOH with respect to citral (1:50) used by us, the content of AcOH (0.5 mol L^{-1}) corresponds to 0.02 mole fractions in H₂O, which is known to be lower than the nonelectrolyte concentration that causes structural variations of the solvent, in particular, the effect of stabilization of the structure of water.^{14,17} Salts at concentrations of $\leq 1 \mod L^{-1}$ in a solvent exist as separate solvated ions that do not destroy the inherent structure of the solvent, though disturb the structure of the solution in the regions adjacent to the local solvation regions.18



Fig. 2. Dependence of the yield of the products of ECH of citral on the proportion of DMF in the solvent: I, citronellol (1); 2, isomeric nerol and geraniol (2) (overall yield).

Thus, allowance for the effect of the solution structure (the "homogeneous" factor) appears to be necessary for conducting preparative-scale electrochemical hydrogenation involving a bulky organic molecule, even in the case where the process has a clear-cut heterogeneous character.

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