Electrochemical hydrogenation of citral. 2*. The effect of the components of the medium on the process of electrochemical reduction at a copper cathode

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The factors (concentration of citral, composition of the solvent, AcOH : citral ratio) affecting electrochemical hydrogenation of citral at an annealed copper cathode have been determined. The highest total yield (94 %) of the alcohols (nerol, geraniol, citronellol) with a considerable predominance of the latter is achieved at 40 % DMF in water, citral concentration 0.02 M, and AcOH : citral ratio = 10:1. The transition to purely organic or purely aqueous media leads to a decrease in both the total yield of the alcohols and the selectivity of the process.

Key words: copper catode, citral, citronellol, electrochemical hydrogenation.

In the previous communication¹ we considered the effect of the state of a copper cathode on the ratio and yield of the products of electrochemical hydrogenation (ECH) of citral. The conditions in which the electrolysis is conducted are known to substantially affect the process of electroreduction (ER) and, consequently, the composition of the products. So, for example, in the ER of 2-thiophenecarboxaldehyde at a mercury cathode the yield of pinacol varies from 16 to 92 % and the d,l/meso ratio of isomers varies from 1 to 12 depending only on the composition of the medium.² A system in which a double bond is conjugated with an electron-withdrawing group is especially sensitive to variations in the conditions of ER, the nature of the cation in the supporting electrolyte and the presence of proton donors. Actually, the main product of the ER of acrylonitrile in aqueous solutions of metal salts is propionitrile, whereas the application of quaternary ammonium salts allows the quantitative preparation of the hydrodimer, adipodinitrile.³ Variation of the water content in DMF dramatically changes the ratio between the products,⁴ and the ER of acrylonitrile in solutions of mineral acids gives the unsaturated amine.⁵

In the present work we have set ourselves the task to find out, the extent to which the ECR of citral is affected by the composition of the medium, when it occurs under conditions,¹ which allow chemisorption of the substrate on the electrode and the formation of

hydrogen in the electrolysis of the acid that is a constituent of the catholyte.

Experimental

The experimental equipment, and the description of the procedures for the electrolysis and quantitative analysis of the products are given in Part 1.¹ The electrolysis was carried out on a copper cathode preliminarily annealed over the flame of a glassblowing burner and then treated with dilute HNO₃ (1 : 10); a saturated calomel electrode was used as the reference electrode.

In all experiments the ratio between nerol and geraniol corresponded to that of neral and geranial in the starting citral, as determined by ¹H NMR spectroscopy.

Results and Discussion

The ER of citral in an ethanol—water mixture (acetate buffer, pH = 5) at a mercury cathode is known⁶ to afford a mixture of two dimers, derivatives of tetrahydrofuran and pinacol, as a result of the interaction of the two enol radicals. However, electrolysis in DMF or in a DMF - 10 % H₂O mixture with tetrabutylammonium perchlorate as the supporting electrolyte at E = -2.2 V gives a complex mixture of dimeric and oligomeric products. In media with low proton-donating activities, radical anions in which the unpaired electron is delocalized over the system of conjugated bonds are probably formed at the high hydrogen overvoltage cathode, as a result of the direct transfer of an electron to the starting

^{*} For Part 1, see Ref. 1

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molecule. The subsequent interaction of the radical anions with the starting compound or with one another gives dimers of various structures and/or oligomers; no monomeric products of the reduction were detected.

Similar products (dimers, oligomers) were obtained as well upon the ER of citral at a copper cathode* in a 40 % DMF-H₂O mixture with 0.1 M KCl as the supporting electrolyte (E = -2.0 V). However, the process conducted in the presence of AcOH (E =-1.2 V, which corresponds to the potential of the evolution of hydrogen) yielded predominantly monomeric products of hydrogenation of double bonds. Since the state of the surface of the copper electrode affects the composition of the products of electrolysis,¹ it may be suggested that the reduction of citral is preceded by its oriented adsorption on the cathode surface. Under the conditions of the experiment the evolution of hydrogen occurs at more positive potentials than the direct reduction of citral. This allows one to assume that the mechanism of the latter reaction consists of the addition of atomic hydrogen to the activated complex on the electrode surface. In the case of 1,2-addition, a mixture of nerol and geraniol (1) is formed, while 1,4-addition gives vinyl alcohol (2), which is converted to the tautomeric aldehyde, citronellal (3).⁷ Under the conditions described, aldehyde 3 is reduced via 1,2-addition of hydrogen to yield citronellol (4). (The formation and the subsequent disappearance of aldehyde 3 in the course of the electrolysis was detected by GLC and TLC; the reduction of allyl alcohols 1 does not occur under these conditions).

The effect of the conditions of the electrolysis on the composition of its products is in agreement with the presumed mechanism of the process and enables the determination of the conditions for the highest yield of citronellol **4**. Judging by the results of the ECH of citral

* The experiments were carried out at a cathode which was not subjected to annealing



Fig. 1. The dependence of the yield of the products of ER of citral on the content of DMF in the DMF- H_2O system: citronellal 3 (1); the sum of nerol and geraniol 1 (2); citronellol 4 (3); the sum of aldehyde 3 and alcohol 4 (4).

Table 1. The yield and the ratio of the products of ECH of citral at an annealed copper cathode as a function of the composition of the solvent (H₂O-DMF) ($C_{citr} = 0.024 M$. $C_{AcOH} = 0.5 M$)

Run	Proportic of DM (vol. %	on E/V F 6)	Time /h	4/1 ratio	The total yield of 1+3+4 (%	Unreacted citral) (%)
1	0	-1.3	2.5	1	54	19
2	5	-1.3	2	1.5	58	19
3	25	-1.2	2.5	1.7	87	
4	40	-1.2	2	2	94	_
5	50	-1.2	2.5	2	76	4
6	75	-1.3	5.5	0.7	49	13
7	100	-1.5	3.5	0.2	28	18



Run	C _{citr.} / M	C _{AcOH} / M	The C_{AcOH}/C_{citr} ratio	Duration of ECH / h	4/1 ratio	The total yield of alcohols (%)
1	0.021	0.084	4:1	2	3.3	77
2	0.021	0.25	10:1	2	4.8	90
3	0.021	0.5	20:1	2	2.3	86
4	0.021	1.0	40:1	2	0.68	53
5	0.042	0.25	5:1	4	3.4	88
6	0.063	0.5	9:1	5.5	3	81
7	0.14	0.5	4:1	14	1.4	90

Table 2. The total yield of alcohols and their ratio as a function of the concentrations of citral and AcOH at 40 % DMF

in DMF-H₂O solutions (see Table 1 and Fig. 1) the formation of alcohol **4** is favored by using the solvent containing 40 % DMF. Water is known⁸ to possess an ordered structure and water clusters do not prevent the interaction of small polar molecules with the electrode surface, however, they hamper the adsorption of bulky organic molecules with long alkyl radicals (for example, citral); this may be the reason for low yields of alcohols in aqueous solutions.

When the solvent contains 50-80 volume % DMF, destruction of water clusters and formation of DMF · H₂O associates occur. If the content of DMF is higher than 80 %, then 2DMF \cdot H₂O associates and their aggregates are formed. This is why the changes in some of the physical properties of DMF-H₂O mixtures are not monotonic. In fact, the maximum viscosity is observed at ~70 % DMF, and the density is maximum at ~50 %.9 Thus, the highest yield of alcohols (see Fig. 1) is observed in the region in which the water structure is destroyed by the increasing proportion of DMF in the mixture, *i.e.*, under conditions favorable to the adsorption of organic molecules on the electrode surface. When the content of DMF is further increased, the solubility of citral in the water-organic phase increases, which naturally lowers its adsorption¹⁰ and, consequently, the yield of alcohols. Competition of a similar character was observed previously^{11*} in the adsorption of water and mercaptan molecules on a copper powder in a water - dibutyl ether medium. As the content of the organic phase increased, the adsorption of mercaptan initially increased and then decreased.

When the electrolysis was carried out in a solution with a higher viscosity (~75 % DMF), it was found that even an increase in the duration of the electrolysis to 5.5 h does not result in the disappearance of the starting citral (Table 1, run 6). Moreover, at the end of the electrolysis the reaction mixture contains substantial amounts of aldehyde 3, though, as has been noted above, in the solutions containing less than 50 % DMF (runs 2-5), citronellal 3 is formed and then disappears in the course of ECH. It was of interest to follow the dependence of the selectivity of the process on the composition of the medium. Since the advent of a type A intermediate complex favors the formation of a mixture of alcohols 1 and that of type **B** leads to alcohol 4and aldehyde 3, the total yield of compounds 4+3 must reflect the possibility of the appearance of state B. It turns out that under conditions in which there is a noticeable lowering of the depolarizer adsorption (100 % DMF or H_2O , the 4/1 or (4+3)/1 ratio is close to unity. In the intermediate region (20-80 % DMF), the (4+3)/1 ratio is approximately two (see Fig. 1), *i.e.*, the selectivity is fundamentally determined by the state of the cathode surface,¹ while the total yield of the products is governed by the composition of the medium. The most favorable medium for the preparation of alcohols proved to be 40 % aqueous solutions of DMF containing KCl as the electrolyte and additions of AcOH.

To determine the optimal conditions for the formation of alcohol 4, we studied the dependence of the composition of the electrolysis products on the concentrations of citral and AcOH in the solution. The stoichiometric ratio of the concentration of AcOH to that of citral, necessary for the hydrogenation of both conjugated multiple bonds, is 4 : 1. The effect of the concentration of AcOH on the yield and ratio of alcohols is presented in Table 2.

We found that more than a twofold excess of AcOH with respect to its required stoichiometric amount results in a nearly quantitative total yield of alcohols (run 2) and relatively high selectivity with respect to alcohol 4. Under these conditions, 94 % of the amount of evolved hydrogen theoretically calculated on the basis of the current, is actually consumed. A further increase in the concentration of AcOH with respect to that of citral leads to a pronounced reduction in both the yield of the alcohols and the selectivity: unsaturated alcohols 1 turn out to be the main products (run 4). It is conceivable that at a great excess of AcOH its adsorption on the cathode surface prevents the efficient interaction of citral with the electrode, so that the formation of the a type B intermediate state is less probable. Surface hydrogenation should obviously be limited by the capacity

^{*} See p. 192

of the electrode, *i.e.*, the number of real active sites on which adsorption with the formation of complexes A or B can occur. Thus, high concentrations of citral can disrupt the adsorption equilibrium and, consequently, lower the yield of the alcohols. So, for example, a threefold increase in the concentration of citral (cf. runs 2 and 6, Table 2) while the ratio between the concentrations of AcOH and citral remains equal to ~10:1 leads to a certain deterioration of the total alcohol yield and the 4/1 ratio. However, in the case of the stoichiometric ratio between the concentrations of AcOH and citral, which is 4:1, a sevenfold increase in the citral concentration does not result in a decrease in the total yield of the alcohols, though the 4/1 ratio is approximately halved. Thus, with an increase in the concentration of citral in the solution and accordingly in the surface layer, the competition for the surface adsorption sites leads to the predominant formation of the type A complex which is less structurally hindered. Establishing a low concentration of the starting citral, when the concentration of AcOH is equal to 0.5 M, by the dropwise addition of 0.021 M of the depolarizer over a period of 1 h does not fundamentally influence the total yield of the alcohols and the 4/1 ratio in the products. Thus, in choosing the conditions for the ECH of citral not only the ratio between AcOH and citral but also their absolute concentrations have been found to be important.

The composition of the reaction mixture in the course of ER (determined by a GLC analysis of the samples) under the conditions of run 6 is significant (Table 2). In the initial 30 min of the electrolysis, synchronously with the decrease in the concentration of citral, some amount of dimers and oligomers is formed. A sample taken after 1 h contains the same amount of dimers and also compounds 1, 3, and 4; the 4/1 ratio is -0.7. At the end of the electrolysis the same amount of dimers is retained, citronellal 3 is scarcely present, and the 4/1 ratio is 3.

Since chemisorption is a slow step, 11* the corresponding products of the ECH of citral are produced only with some time. Alcohol 1 and aldehyde 3, which

* See p. 210.

result from one-step hydrogenation, are formed initially, and then alcohol 4, the product of two-step hydrogenation, is formed. It should be noticed that the ratio between compounds 4 and 1 in the bulk of the solution gradually increases and reaches the value given in Table 2 only at the close of the process.

Thus, we have experimentally determined the conditions under which only ECH of citral, rather than direct ER, occurs at a copper cathode to give a mixture of alcohols in 90 % total yield, and citronellol is the substantially prevailing product (the content of unsaturated alcohols is ~16 %).

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