Electrochemical hydrogenation of citral 4.* Role of the acid component in electrochemical hydrogenation

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The effect of the nature and concentration of the acid component on the yield and ratio of the products of electrocatalytic hydrogenation of citral was studied. The use of weak organic acids (e.g., AcOH) in amounts that are stoichiometric for hydrogenation of conjugated double bonds was shown to be advantageous.

Key words: citral, electrocatalytic hydrogenation, copper cathode, acid component.

The electrocatalytic hydrogenation (ECH) of an unsaturated compound presumes that a potential source of hydrogen, *i.e.*, an acid component, is present in the solution. Like other compounds containing a system of conjugated C=C and C=O bonds, citral, a model compound that we have used in studies of electrocatalytic hydrogenation,¹⁻³ can undergo chemical transformations such as vinyl polymerization, condensation, as well as 1,2-, 1,3-, and 1,4-addition of H₂O and HCl, in the presence of acids and bases.⁴

The choice of acids that can be used for electrocatalytic hydrogenation is quite limited due to the lability of the organic substrate; in addition, the nature and concentration of the acid component can considerably affect the pathway and result of electrocatalytic hydrogenation.

The present communication considers this problem in detail.

Experimental

The experimental techniques and procedures for electrolysis and quantitative analysis of the products have been reported elsewhere.²

Polarographic studies were carried out on a PU-1 polarograph using the three-electrode scheme of cell connection (mercury dropping electrode ($m = 1.94 \text{ mg} \cdot \text{s}^{-1}$, t = 0.3 s), bottom mercury, saturated calomel electrode as the reference).

Electrolysis of citral in the presence of acids was carried out on a copper cathode that had been previously annealed in the flame of a glass-blowing burner and treated with dilute HNO_3 (1 : 10). A saturated calomel electrode was used as the reference, and 40 % aqueous DMF was used as solvent. It was established by GLC and ⁻¹H NMR spectroscopy that in all experiments, the ratio of the yields of nerol and geraniol corresponded to the ratio of their concentrations in the starting citral.

Results and Discussion

Polagrographic studies showed that citral gives one one-electron wave with $E_{1/2} = -1.91$ V in DMF if 0.1 *M* tetrabutylammonium iodide (TBAI) is used as the supporting electrolyte. The addition of water gives rise to the appearance of two one-electron waves; the $E_{1/2}$ value of the first wave is shifted in the positive direction. In 40 % DMF, $E_{1/2}^{I} = -1.52$ V and $E_{1/2}^{II} = -2.08$ V (Fig. 1, curve *I*).

A change in the content of water in an organic solvent changes the diffusion coefficient of a depolarizer, its adsorption on an electrode, and the acid-base properties of the medium, etc.⁵ In the case considered. an increase in water content may lead to an increase in the solvation energy of the depolarizer, and thus the addition of an electron to form a radical anion occurs at a more positive potential. When AcOH is added to this solution in a less than equimolar amount, $E_{1/2}$ of the first wave is additionally shifted by 70 mV to positive potentials (Fig. 1, curve 2), and the limiting current i_{lim} of the wave does not change although its slope increases. In this case, the i_{lim} of the second wave, its slope, and $E_{1/2}$ remain practically unchanged. It is noteworthy that the discharge wave of protons from AcOH is absent, and that a small wave ($E_{1/2} = -1.7$ V) appears only in the case when more than an equimolar amount of the acid is used.

It is known⁶ that carbonyl compounds form associates with organic acids in aprotic media. Effects explained by the formation of similar associates have also been observed in an aqueous medium.⁷ The data obtained by us make it possible to assume the formation of such associates between citral and acetic acid. The

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Fig. 1. Polarograms of citral ($C = 6.6 \cdot 10^{-4} \text{ mol} \cdot L^{-1}$) in DMF (40%) with 0.1 *M* TBAI as supporting electrolyte in the absence (*I*) and in the presence of AcOH (2), HCl (3), H₂C₂O₄ (4), H₃BO₃ (5). *C*/mol $\cdot L^{-1}$: 3.3 $\cdot 10^{-4}$ (2-4); 6.6 $\cdot 10^{-4}$ (5).

absence of a hydrogen discharge wave when the amount of AcOH is less than equimolar implies rather strong complexation of the acid with citral. Since both the first and second waves practically do not change, one may assume that protonation of the radical anion does not occur. With a twofold excess of AcOH, the second wave disappears (the $E_{1/2}$ of the first wave remains unchanged); this may indicate dimerization of the radical anions (or their associates with AcOH) that are formed during the first wave in the bulk of the solution.

Another picture is observed in the presence of HCl in 40% DMF containing citral. When only half of an equimolar amount of HCl is added, one wave with $E_{1/2} = -1.05$ V (Fig. 1, curve 3) and a hydrogen discharge wave with $E_{1/2} = -1.45$ V can be seen. In the case of completely dissociated HCl, preceding protonation of citrai (shift of $E_{1/2}$ to the positive region) apparently takes place, which should inevitably cause successive chemical transformations of the free radical particles in the bulk of the solution.

The polarograms of citral solutions in anhydrous DMF in the presence of HCl and AcOH are also different. The addition of an equimolar amount of AcOH results only in a shift of the one-electron wave of citral by ~ 100 mV to the positive region, whereas only a wave whose potential coincides with that of hydrogen ion discharge is observed upon the addition of the same amount of HCl.

At first glance, a picture similar to that described for the addition of HCl to citral solution in 40 % DMF (Fig. 1, curve 4) is observed in the presence of oxalic acid. However, the height of the hydrogen evolution wave $(E_{1/2} = -1.51 \text{ V})$ is noticeably lower in the presence of citral than in its absence. The ambiguous effect of oxalic acid may result from the presence in its molecule of two carboxyl groups whose dissociation constants differ by three orders of magnitude. When a small amount of oxalic acid is added, dissociation of one carboxyl group probably occurs in solution, resulting in preceding protonation of citral and its resinification. The monoanions of oxalic acid that form are bound in associates with citral, similarly to other organic acids, leading to a decrease in the height of the hydrogen discharge wave.

When an equimolar amount of H_3BO_3 is added, the polarographic curve of citral in 40% DMF changes insignificantly: $E_{1/2}$ of the first wave shifts 40 mV to the positive region and i_{lim} of the second wave ($E_{1/2} =$ -2.15 V) increases by a value that approximately corresponds to the height of the hydrogen evolution wave for H_3BO_3 (Fig. 1, curve 5).

Thus, the polarographic data considered above indicate that citral interacts in diverse ways with the acid components of the medium both in the near-electrode layer and in the bulk of the solution.

Although ECH occurs on the electrode surface between an adsorbed molecule of an organic substrate and adsorbed hydrogen evolved during an electrochemical reaction,⁸ ECH must inevitably reflect the preceding chemical reactions of citral in the bulk of the solution. Taking into account the chemical features of our object and the polarographic data, the weak organic acid AcOH seems to be the most suitable for ECH.

Unlike on a mercury cathode, hydrogen discharge from AcOH on an annealed copper cathode² occurs at E = -1 to -1.2 V, *i.e.*, the potential is more positive than that of direct reduction of citral, which allows one to carry out ECH. The potential of maximum adsorption of organic compounds on a copper cathode in an aqueous medium is approximately -1.1 V (with respect to a saturated calomel electrode),⁹ that is, the adsorption of aliphatic compounds is high within the -0.9 V to -1.4 V interval.

Earlier² we showed that the main products of ECH of citral on an annealed copper cathode in the presence of AcOH are alcohols, such as citronellol (1) and the isomeric compounds nerol and geraniol.



We carried out a series of electrolyses in the presence of different amounts of AcOH under optimal condi-



Fig. 2. Plot of the ratio of the alcohols 1/2 vs. acetic acid concentration at ECH of citral in 40 % aqueous DMF solution on an annealed copper cathode (the total yield of alcohols 1 and 2 was 70–90 % within the whole range on the acid concentration).

tions³ (40% DMF). The total yield of the products appeared to be rather high (75–90 %) in a wide range of AcOH concentrations (up to a 20-fold excess with respect to citral). Figure 2 shows the change in the process selectivity as a function of the amount of AcOH in solution.

Under these conditions, the evolution of hydrogen occurs even in the absence of an acid but at a somewhat more negative potential (-1.5 to -1.6 V). The total yield of the products is also high in this case (~90 %), although the ratio of the alcohols (1/2) is close to one. On a non-annealed copper cathode³ in the absence of AcOH, direct reduction of citral mainly occurs at E = -1.8 to -1.9 V, whereas the addition of AcOH results in a decrease in the ECH potential to -1 to -1.2 V and an increase in the selectivity of the process. The maximum selectivity is reached when the amount of acid stoichiometrically necessary for complete hydrogenation of the system of conjugated bonds C=C-C=O is present ($C_{AcOH}/C_{citr} = 4/1$).

AcOH is a depolarizer, i.e., a source of hydrogen for hydrogenation in the ECH process. On the other hand, it follows from the polarographic data that AcOH takes part in the formation of stable associates with citral. It is quite probable that adsorption of these associates, which are simultaneously a source of hydrogen, on the copper electrode surface leads to an increase in the selectivity of hydrogenation (owing to the proximity of reaction centers). However, increasing the AcOH concentration results in a gradual decrease in the selectivity of ECH (see Fig. 2), which may be due to the displacement of citral from the electrode surface by adsorbing AcOH molecules.¹¹ With a large excess of AcOH, blocking of the electrode surface becomes possible, decreasing both the alcohol yields and the selectivity of the process.³ (With the ratio $C_{ACOH}/C_{citr} = 40/1$, the total yield of the alcohols is 53%, while the ratio of alcohols 1/2 is 0.68.)

We carried out ECH in the presence of other organic acids, namely, formic and propionic acids, using the optimal ratio of the acid and citral concentrations (4/1) (Table 1, entries 2 and 3).

Table	1. 7	fotal	yield	and	ratio	o of	the	products	of electr	ochemi-
cal hy	ydroj	genat	ion (of ci	tral	on	an	annealed	copper	cathode
(c = 0)	0.024	1 mo	1.L-	1, 40)% a	que	ous	DMF as	the solve	ent)

En	try Acid	E/V	C/co	Yield ^b		ac
				1+2(%)	1/2	(%)
1	нсоон	$-0.8 \div -0.9$	4	86.0	4.3	
2	CH ₃ CH ₂ COOH	$-1.0 \div -1.1$.4	84.5	3.0	·
3	HCI	$-0.6 \div -0.7$	4	34.2	0.3	12.4
4	HCId	$-0.6 \div -0.7$	10	28.5	0.1	12
5	H ₁ BO ₁	$-1.4 \div -1.6$	4	57.5	1.7	4.8
6	HOOC-COOH	$-0.7 \div -1.0$	4	45.0	0.3	6.4
7	HOOC-COOH	$-0.7 \div -1.0$	2	33.2	0.4	3.2

^a C is acid concentration, c is citral concentration.

^b I is citronellol, 2 is a mixture of nerol and geraniol.

° 50 % aqueous DMF.

 $d \alpha$ is the unreacted original compound.

Although the yield of the products and the selectivity of the process are rather high with all three organic acids, one can see the tendency of these parameters to decrease as the size of the organic acid molecule increases, which may be due to an increase in its adsorption.

According to the results of polarographic studies, one would hardly expect the efficiency of the ECH of citral in the presence of HCl to be high. The process is indeed accompanied by significant resinification, the yield of alcohols 1 and 2 is low (Table 1, entries 3 and 4), and a noticeable amount of the original citral remains unreacted, although the amount of electricity passed (Q) is almost twice as high as that required theoretically for the complete hydrogenation of the conjugated system $(Q_{exp} \sim 0.2 \text{ A} \cdot h; Q_{calc} = 0.128 \text{ A} \cdot h)$. Evolution of hydrogen occurs in this case at a more positive potential than in the presence of AcOH.

Similar results were also obtained in the presence of oxalic acid (Table 1, entries 6 and 7). However, according to the data of a GLC analysis of the reaction mixture at high column temperatures, significant amounts of side products were formed along with alcohols 1 and 2.

We tried to isolate and identify some of these products. Separation on a SiO₂ column (gradient elution from hexane to ether) afforded, along with alcohols 1 and 2, three more fractions with smaller R_f (0.17, 0.15, and 0.07, GLC, ether : hexane = 1 : 1). Each of the fractions appeared to be a complex mixture of isomers. The total amount of the fractions isolated was 25 % of that of the initial citral taken into the reaction. The chromatographic behavior and the mass spectra of the fractions indicate the dimeric character of the products formed. Although molecular ion peaks corresponding to dimers were not recorded, signals with m/z 183 and 205 were present. It should be noted that the molecular mass of citral is 152 and the cleavage of the C—C bond near the oxygen atom, which is most typical of the dimeric molecule, results in elimination of an ion with m/z 123. In addition, all of the spectra contain groups of peaks with m/z 154, 155, and 157 in different ratios, and all signals typical of fragmentation of alcohols 1 and 2 are simultaneously present in the region with m/z <154.

The IR spectra of all three fractions show a broad intense band at 3330 cm⁻¹ corresponding to O-H stretching vibrations and also a moderately intense band of the carbonyl group near 1720 cm⁻¹. The spectrum contains also a medium-intensity band at 1660 cm⁻¹ typical of substituted olefins.

The characteristic feature of the ¹H NMR spectra of the isolated fractions is the presence of a signal of the proton at the double bond with the OH-group in the β -position (5.4 ppm); the signals at 5.1 ppm corresponding to the proton of the terminal double bond are insignificant.

These data allow one to conclude that the side products of ECH are dimers in which the monomeric fragments with different degrees of hydrogenation are linked "head-to-tail", *i.e.*, with the participation of the isolated double bond. It should be noted that the electrochemical reduction of geranial¹¹ on a mercury cathode in an aqueous-alcoholic acetate buffer (pH = 5) afforded two dimers in 60% yield, a hydroxytetrahydrofuran derivative and a glycol, *i.e.*, both "head-tohead" isomers. However, in the case of ECH, although such isomers can also be present in the reaction mixture, "head-to-head" type dimerization is evidently not the principal direction.

Earlier we showed that ECH of citral on a copper cathode in the presence of AcOH does not affect the isolated double bond.^{2,3} In the presence of strong acids, however, the transition of the first electron occurs at a potential close to that of hydrogen discharge due to the preceding protonation of citral. Since the potential on the copper cathode in this case is more positive than the potential of maximum adsorption of the organic compound, the radical is able to leave the cathode surface and react with the original citral in the bulk of the solution, *i.e.*, dimerization can occur. In this case, the isolated double bond may appear to be more available for attack by the radical. Such dimerization cannot be selective, *i.e.*, stereo- and structural isomers must be formed. In addition, the process can be accompanied by cyclization, migration of double bonds, etc. Another reason for the existence of large amounts of isomers is the use of a mixture of neral and geranial as the initial reagent. The formation of only trace amounts of dimers in the presence of a stronger acid (HCl) can probably be explained by resinification of citral in the solution during the electrolysis. Another possible pathway of the transformation of the radicals is their subsequent reduction (transfer of the second electron) on the cathode surface to give an unsaturated alcohol. The direct reduction of citral takes place in parallel to ECH in the presence of strong acids. This is probably the reason for the preferential formation of alcohol 2.

The ECH of citral proceeds worse in the presence of boric acid (Table 1, entry 5) than in the presence of organic acids; the total yield of alcohols and the selectivity are substantially lower than with AcOH. A weak acid that does not dissociate under these conditions may be adsorbed on to the electrode surface, thus preventing the effective adsorption of citral.

It should be stressed that in any case changes in the nature of the acid play a more important role than changes in acid concentration. In fact, for strong acids, changing their concentration from the stoichiometrically necessary amount to larger values (for HCi, see Table 1, entries 3 and 4) or to smaller values ($H_2C_2O_4$, Table 1, entries 6 and 7) has practically no effect on the yield and ratio of the products. In the case of weak organic acids, the yield of the products and the selectivity of the process remain high for a wide range of acid concentrations.

Thus, the nature of the acid plays a decisive role in the ECH. In general, the use of weak organic acids (AcOH) in amounts corresponding to stoichiometric for hydrogenation of conjugated double bonds is advantageous.

References

- T. Ya. Rubinskaya, L. M. Korotaeva, and V. P. Gul'tyai, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 82 [*Russ. Chem. Bull.*, 1996, **45**, 74 (Engl. Transl.)].
- L. M. Korotaeva, T. Ya. Rubinskaya, and V. P. Gul'tyai, Izv. Akad. Nauk, Ser. Khim., 1993, 1915 [Russ. Chem. Bull., 1993, 42, 1830 (Engl. Transl)].
- T. Ya. Rubinskaya, L. M. Korotaeva, and V. P. Gul'tyai, Izv. Akad. Nauk, Ser. Khim., 1993, 1919 [Russ. Chem. Bull., 1993, 42, 1835 (Engl. Transl.)].
- A. N. Nesmeyanov and N. A. Nesmeyanov, Nachala organicheskoi khimii [Basics of Organic Chemistry], Khimiya, Moscow, 1969, 1, 316 (in Russian).
- A. P. Tomilov, S. G. Mairanovskii, M. Ya. Fioshin, and V. A. Smirnov, Elektrokhimiya organicheskikh soedinenii [Electrochemistry of Organic Compounds], Khimiya, Leningrad, 1968, 68 (in Russian).
- 6. B. Paduszek-Kwiateb and M. Kalinowski, *Electrochim.* Acta., 1984, 29, 1439.
- S. G. Mairanovskii, M. K. Beisembaeva, and E. A. Mambekaziev, *Elektrokhim.*, 1992, 25, 1245 [Sov. *Electrochem.*, 1992, 25 (Engl. Transl.)].
- G. Horanyi and K. Torkos, J. Electroanal. Chem., 1980, 111, 279.
- J.O'M. Bocris and D. A. J. Swinkels, J. Electrochem. Soc., 1964, 111, 736.
- G. Horanyi and E. M. Rizmayer, J. Electroanal. Chem., 1983, 159, 195.
- J. C. Johnston, J. D. Faulkner, L. Maudell, and R. A. Day, J. Org. Chem., 1976, 41, 2611.

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