persulfonic acid is due to the accumulation of the corresponding sulfonic acid, whose yield (calculated per decomposed peracid) is ~85% (343 K, $[RSO_2OOH]_0$ = $2.1 \cdot 10^{-2}$ mol L^{-1}). When hydrocarbons are added to the reaction mixture, the yield of sulfonic acid reaches the quantitative value.[1] The kinetic regularities of the reaction can be explained in terms of the following formal scheme:

$$RSO_2OOH \longrightarrow RSO_2OH + 1/2\ O_2, \qquad (1)$$

$$RSO_2OOH + RSO_2OH \longrightarrow 2\ RSO_2OH + 1/2\ O_2. \qquad (2)$$
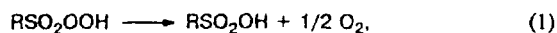
According to this scheme, the consumption of the persulfonic acid can be described by the equation

$$d[RSO_2OOH]/dt =$$
$$= -k_1[RSO_2OOH] - k_2[RSO_2OOH] \cdot [RSO_2OH],$$

where k_1 and k_2 are the rate constants of the corresponding stages.

Under the experimental conditions, when $[HX]_0 \gg [RSO_2OOH]_0$, the accumulation of sulfonic acid at the initial stages of the reaction can be neglected. After integration, we obtain the expression

$$\ln([RSO_2OOH]_0/[RSO_2OOH]) = (k_1 + k_2[HX])t$$

($[HX]$ is the concentration of sulfonic or other acid).

Taking into account that $k_1 + k_2[HX]$ is, in fact, the experimental rate constant of consumption of persulfonic acid, i.e.,

$$k_{exp} = k_1 + k_2[HX],$$

we can expect a linear dependence of k_{exp} on the content of acids in the system, which is observed experimentally (see Table 1). According to this equation, we found from the dependences of k_{exp} on $[HX]$: $k_2(70\ ^\circ C)$ = $(4.3\pm0.5) \cdot 10^{-3}$ L $(mol\ s)^{-1}$, r = 0.998 for cyclohexanesulfonic acid and $k_2(70\ ^\circ C)$ = $(1.8\pm0.6) \cdot 10^{-2}$ L $(mol\ s)^{-1}$, r = 0.999 for trifluoroacetic acid. It is found from the intercepts on the Y axis: $k_1(70\ ^\circ C)$ = $(2.7\pm0.5) \cdot 10^{-5}$ s^{-1} and $(2.9\pm1.1) \cdot 10^{-5}$ s^{-1} at HX = $C_6H_{11}SO_2OH$ and CF_3COOH, respectively. These k_1 values agree well with the k_{exp} values determined from the initial regions of the kinetic curve of consumption of RSO_2OOH (see Table 1) in the absence of acids in the starting mixture when reaction (2) can be neglected.

References

1. R. L. Safiullin, R. N. Zaripov, A. A. Elichev, S. Yu. Serenko, and V. D. Komissarov, *Kinet. Katal.*, 1990, 31, 808 [*Kinet. Catal.*, 1990, 31 (Engl. Transl.)].
2. A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, *Technique of Organic Chemistry*, VII, *Organic Solvents. Physical Properties and Methods of Purification*, Interscience Publishers, Inc., New York, 1955.
3. V. L. Antonovskii and M. M. Buzlanova, *Analiticheskaya khimiya organicheskikh peroksidnykh soedinenii* [*Analytical Chemistry of Organic Peroxide Compounds*], Khimiya, Moscow, 1978 (in Russian).

Electrochemical hydrogenation of citral

6.* Voltammetric measurements in DMF solutions of citral and acetic acid

V. P. Gultyai[a] *and V. V. Strelets[b]*

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: gv@cacr.ioc.ru
[b]*Institute for Chemical Physics Research, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588

The electrochemical behavior of citral at Hg, Au, Pt, Cu, and glassy carbon electrodes was studied by cyclic voltammetry in DMF solutions containing acetic acid. Electrocatalytic hydrogenation of citral is the predominant reaction route at Pt and Cu electrodes.

Key words: citral, electrocatalytic hydrogenation, cyclic voltammetry.

Despite the substantial interest in the preparative electrochemical reduction of citral (Cit) both in aqueous

alcohols[2] and aqueous DMF,[3,4] the mechanism of its electroreduction, unlike those of other α,β-unsaturated carboxyl compounds,[5] has not been studied. The purpose of this work is to study this aspect and to verify the

---

* For Part 5, see Ref. 1.

previous hypothesis[4] concerning the mechanism of the electrocatalytic hydrogenation of Cit in the presence of AcOH.

Under conditions of cyclic voltammetry, citral in DMF undergoes diffusion-controlled ($I_p \cdot v^{-1/2}$ = const, where I_p is the peak height, and v is the linear potential sweep rate) irreversible one-electron reduction. The reduction peak of Cit in the v = 0.01—0.5 V s^{-1} range remains irreversible even when the temperature decreases to −55 °C. The conclusion that the reduction is a one-electron process is based on a comparison of the

Fig. 1. Voltammetric curves of hydrogen evolution (broken lines) at GC (*a*), Hg (*b*), Cu (*c*), and Pt electrodes (*d*) in DMF/0.05 *M* Bu$_4$NPF$_6$ in the presence of AcOH (8·10^{-3} mol L^{-1}). Cyclic voltammogram of Cit (1·10^{-3} mol L^{-1}) at a Cu electrodes (dashed line) in anhydrous DMF/0.05 *M* Bu$_4$NPF$_6$. Continuous lines correspond to the background curves; current is expressed in relative units; v = 0.2 V s^{-1}; 20±2 °C.

height of this peak with that of the peak of reversible one-electron reduction of acetophenone,[6] all other factors being the same. In the absence of proton donors (AcOH, H$_2$O), the potential of the reduction peak of Cit (E_p) varies from −2.03 to −2.05 V (*vs* s.c.e.) and virtually does not depend on the electrode material (Hg, glassy carbon (GC), Au, Cu, Pt). This apparently indicates that an electron is reversibly transferred to the Cit molecule and the resulting Cit·⁻ radical anion undergoes a fast chemical transformation (*EC* scheme, where *E* and *C* are the electrochemical and chemical steps, respectively); this is consistent with the data on the electrochemical behavior of 2-cyclohexenones.[5] More detailed investigation of the possible transformations of Cit·⁻ in an aprotic medium was beyond the scope of our study; however, by analogy with the published data,[5] it can be assumed that the main pathway in which the radical anion decays is hydrodimerization as the subsequent irreversible chemical step.

Previously it has been found[3,4] that the selectivity of the electroreduction of Cit depends substantially on the nature of the electrode material, its heat pretreatment, and the composition of the medium. The most efficient electroreduction of Cit to give citronellol and unsaturated alcohols (nerol and geraniol) is attained at an annealed Cu electrode in aqueous DMF containing AcOH.[3,4] However, electrolysis of solutions of Cit in DMF and aqueous DMF at potentials corresponding to the limiting current of the wave of its reduction affords a complex mixture of dimers and oligomers.[4] It has been suggested[3,4] that reduction of Cit at a Cu cathode in the presence of proton donors (AcOH, H$_2$O) follows a mechanism of catalytic hydrogenation involving electrochemically generated hydrogen. Therefore, it was of interest to compare voltammetric curves (VC) for hydrogen evolution at various electrodes (Fig. 1).

For comparison, this figure also shows the VC of the supporting electrolyte (DMF/0.05 *M* Bu$_4$NPF$_6$) at various electrodes and also the peak of Cit reduction (the vertical dashed line marks the reduction potential). It can be seen that even upon the addition of 8·10^{-3} mol L^{-1} of AcOH, the potentials of hydrogen evolution depend significantly on the nature of the electrode material and shift to the anodic region in the series Hg < GC < Au (not shown in Fig. 1) < Cu* < Pt. When the solution contains >10% (v/v) water, the potentials of hydrogen evolution at all of the electrodes studied shift to the anodic region to even a greater extent (to 0.3—0.5 V). Therefore, the results obtained cannot be completely compared with the results of previous studies;[3,4] however, qualitative conclusions can be drawn. In the case of Hg and GC electrodes, the reduction peak of Cit can be observed even at a tenfold excess of AcOH (with respect to Cit), whereas at other electrodes studied, this
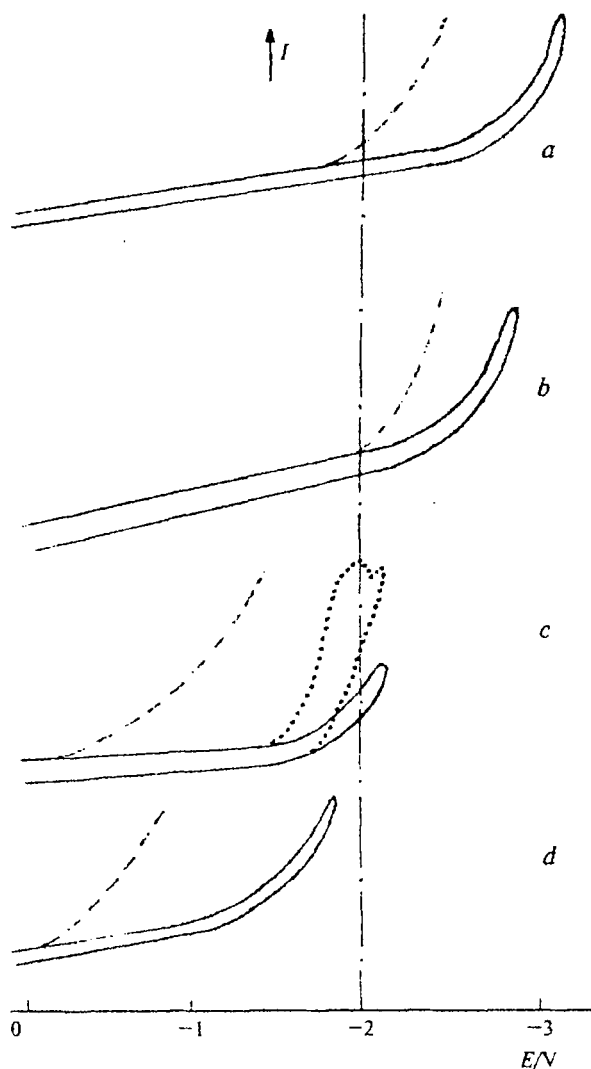
---

* The microelectrode can be regarded as annealed because the sealing of copper in glass was carried out at temperatures of ≥500 °C.

peak is masked by the current of hydrogen evolution, which occurs at less cathodic potentials.

The above-presented results support the assumption that at sp electrodes characterized by high hydrogen overvoltage (Hg, GC), reduction of citral even in the presence of slight amounts of proton donors occurs apparently (at least, as a competing process) via the intermediate formation of unstable Cit$^{\cdot-}$ radical anion and, as a consequence, the formation of hydrodimers and resinification products. However, hydrogen evolution at Cu and especially Pt electrodes in the presence of proton donors in the electrolyte solution mainly follows an electrocatalytic pathway. It can be assumed that this process predominates at a Pt electrode, whereas at a Cu cathode, catalytic hydrogenation of Cit is the main reaction pathway.

Thus, in our opinion, the data of electroanalytic studies confirm the previously made[3] suggestion that the electroreduction of citral at cathodes with medium hydrogen overvoltage (e.g., Cu) occurs as an electrocatalytic process, apparently, according to the 1,2-and 1,4-addition mechanism.

Experimental

Voltammetric measurements were carried out in a dry inert atmosphere and in DMF, which was purified preliminarily by a standard procedure[6] and transferred without contacting with air into an evacuated electrochemical cell filled with argon, as described previously.[7] A 0.05 M solution of Bu_4NPF_6 was used as the supporting electrolyte. Tetrabutyammonium hexafluorophosphate (Aldrich) was dehydrated prior to use by melting in vacuo. Low-temperature electrochemical measurements were carried out in a cell maintained at a constant temperature by isopropyl alcohol cooled with liquid nitrogen in a Dewar flask.

References

1. L. M. Korotaeva, T. Ya. Rubinskaya, and V. P. Gul'tyai, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1531 [*Russ. Chem. Bull.*, 1998, **47**, 1487 (Engl. Trans.)].
2. J. C. Johnston, J. D. Faulkner, L. Mandell, and R. A. Day, *J. Org. Chem.*, 1976, **41**, 2611.
3. 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.)].
4. T. Ya. Rubinskaya, L. M. Korotaeva, and V. P. Gul'tyai, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1915 [*Russ. Chem. Bull.*, 1993, **42**, 1835 (Engl. Transl.)].
5. P. Margaretha and P. Tissot, *Nouv. J. Chem.*, 1979, 3, 13.
6. V. P. Gul'tyai, L. M. Korotaeva, A. S. Mendkovich, and I. V. Proskurovskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 834 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, 30 (Engl. Transl.)].
7. V. V. Strelets, and K. J. Pikket, *Elektrokhimiya*, 1994, 30, 1023 [*Russ. Electrochem.*, 1994, **30** (Engl. Transl.)].