

ELECTRODIC PROCESSES OF 2,2,4,4 - TETRAMETHYLPENTANE  
DERIVATIVES ON STATIONARY SOLID ELECTRODES. II.  
VOLTAMMETRY OF 3,3'- DIBROMO - 2,2,4,4 - TETRAMETHYL -  
PENTANE IN DMF

By

H. SCHOLL AND P. KRZYCZMONIK

Institute of Chemistry, Łódź University  
Narutowicza 68, 90 136 Łódź, POLAND

*(Received 1 July 1988)*

The electrodic processes of geminal 3,3'-dibromo-2,2,4,4-tetramethyl pentane in DMF solution, with tetrabutylammonium perchlorate as supporting electrolyte, were examined by means of cyclic voltammetry and controlled potential electrolysis on glassy carbon, platinum and gold electrodes. The reaction products were examined by using HPLC, gas chromatography and <sup>1</sup>H NMR methods.

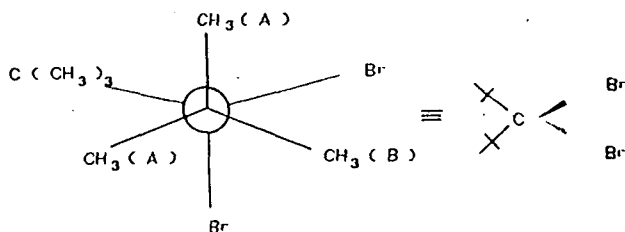
As a result of the electroreduction processes, monobromide and simple aliphatic compounds were obtained in two-stage processes with

$E_{p,c}^1 = -1.00$  V and  $E_{p,c}^2 = -2.00$  V vs AgCl (KCl<sub>sat</sub>, H<sub>2</sub>O), Ag reference electrode.

The complex processes of electrooxidation ( $E > +1.00$  V) probably lead to the formation of the radical cation BTMP<sup>•+</sup> and TMP<sup>++</sup>, which are strongly solvated in DMF or form ionpairs with the appropriate anions of the supporting electrolyte.

## Introduction

Geminal tetramethylpentane dibromide (DBTMP) was subjected to cyclic voltammetry experiments and controlled potential electrolysis. It is a white, crystal line compound with  $T_{mp} = 448 \text{ K}$ ,  $\delta^1\text{H NMR}$  (303 K, TMS,  $\text{CDCl}_3$ ) = 1.49 nm and  $\delta^{13}\text{C NMR}$  = 110.1 nm. Its synthesis was described by Maier and Kalinowski [1].



Scheme I

DBTMP is an aliphatic geminal dihalide, which are characterized by strong steric stresses. The  $\delta^{13}\text{C NMR}$  of geminally substituted carbon atom in halogen derivatives shows deviations ( $\delta_{exp} - \delta_{calc}$ ) that increase with increase of the substituent size. Halogen derivatives of this type are thought to be very good models to illustrate the influence of the  $\gamma$  effect caused by chlorine atoms [1-4].

In the series  $\text{I} \rightarrow \text{Br} \rightarrow \text{Cl}$ , the  $\gamma$  effect on the atom of the (B) *gauche* methyl group to two halogen atoms decreases in the given series (13.4  $\rightarrow$  3.7  $\rightarrow$  1.7 ppm). The effect on the carbon atoms of the (A) methyl groups in Scheme I changes in the same direction (6.0  $\rightarrow$  3.7  $\rightarrow$  3.5 ppm) [1].

Geminal dihalides were earlier examined polarographical-

ly [2-4]. In this work we study the electrodic processes of DBTMP on stationary solid electrodes in N.N-dimethylformamide (DMF). We used cyclic voltammetry (CVC) and controlled potential electrolysis (CPE), supplemented with high-pressure liquid chromatography (HPLC), gas chromatography (GC) and  $^1\text{H}$  NMR spectrometry.

### *Experimental*

CVC and CPE were carried out with the typical apparatus:  
 - a PG-30/1 potentiostat with an LSG programming generator (ASP UL. Poland) and an EMG 79 812 XY recorder (Hungary) for the measurements conducted in Lodz University;

- a Wenking ST-72 potentiostat with a VSG-72 programming generator and Houston Instruments-2000 XY recorder in University of Giessen.

In CVC the measurements were conducted in the range of sweep potential polarization rate from  $v = 0.010 \text{ Vs}^{-1}$  to  $v = 0.300 \text{ Vs}^{-1}$  in the hermetic, thermostatic ( $298 \pm 0.5$ ) K three-electrode vessel of  $90 \text{ cm}^3$  volume made by METROHM.

The following working electrodes was used:

- A polished carbon electrode (GCE) SIGRI with geometrical surface  $A_1 = (0.38 \pm 0.02) \text{ cm}^2$ , polished with diamond paste of 30, 6, 3 and  $1 \mu\text{m}$  and then with  $\text{Al}_2\text{O}_3$  of  $0.05 \mu\text{m}$  and prepared for the measurements according to the literature [5-8];
- a polished platinum electrode ( $\text{Pt}_{\text{pol}}$ ) with geometrical area  $A_2 = (0.38 \pm 0.02) \text{ cm}^2$ , prepared in the same way as the GCE;

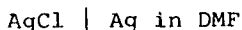
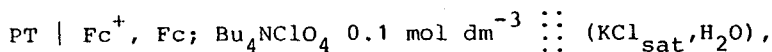
- a gold electrode ( $Au_{app}$ ) with geometrical area  $A_3 = (0.09 \pm 0.02 \text{ cm}^2)$ . prepared for the measurements by means of the "electrochemical sweep" method in an aqueous solution of  $HClO_4$  ( $0.5 \text{ mol dm}^{-3}$ ).

After production of the model polarization curve [9, 10] the reproducibility of the measurements was within the limits  $\pm 0.5 \%$  [11]. The stabilized surface of the gold electrode has the surface development coefficient 4.2 referred to the surface of the polished gold electrode [12]. In this way, the real surface of the  $Au_{app}$  is close to the surface areas  $A_1$  and  $A_2$ .

In the CPE method, a gold electrode ( $A_{4,geom} = 26 \text{ cm}^2$ ) and a platinum electrode ( $A_{5,geom} = 46 \text{ cm}^2$ ) were used, which were prepared for the measurements in the same way as  $Au_{app}$ .

In the measurements  $AgCl(KCl_{sat}, H_2O)$ ,  $Ag$ , METROHM was used as a reference electrode and the potential values given in this work refer to this electrode.

In order to permit comparison of the obtained potential values with the results obtained in other solvents, the CVC curve in the following system was registered:



This led to  $E_f^{DMF} = 0.450 \text{ V}$ , in accordance with literature [13].

Thus, the reference here is to the "ferrocene potential scale" [14, 15]. Although this is not regarded as perfect [16, 17], it is commonly used in the electrochemistry of non-aqueous solvents.

DBTMP readily undergoes hydrolysis. Accordingly, DMF was used after distillation according to the commonly used

methods [18];  $\text{Bu}_4\text{N}^+\text{ClO}_4^-$  dried in vacuum, served as supporting electrolyte. The solutions of the examined substance were kept for 48 hours over molecular sieve 4 Å. Then solutions were then forced through to the measurement cell by using dry argon. The concentrations of DBTMP for CVC were:  $8.7 \cdot 10^{-4}$ ,  $1.1 \cdot 10^{-3}$ ,  $3.3 \cdot 10^{-3}$ ,  $5.0 \cdot 10^{-3}$  and  $7.4 \cdot 10^{-3}$   $\text{mol} \cdot \text{dm}^{-3}$ , while for CPE  $1.25 \cdot 10^{-2}$   $\text{mol} \cdot \text{dm}^{-3}$  solution was used.

Analysis of the CVC curves was carried out according to Nicholson and Shain [19-21] and the electric charge used was determined by means of the CPE method from the dependence  $I = f(t)$ .

The products of the reaction was examined by HPLC with a Zeiss-PM-2 DL spectrometer and a Knauer refractometer with Spectra Physics instrumentation. After n-pentane extraction, the reaction products were further identified by GC with a Varian-aerograph-1400 with a Spectra Physics-autolag system I integrator. For  $^1\text{H}$  NMR spectrometry, a Varian T-60 was used.

### *Results and discussion*

The polarization potential ranges for the supporting electrolyte were: GCE: - 2.65 to +1.45 V;  $\text{Pt}_{\text{pol}}$ : -2.0 to +1.40 V;  $\text{Au}_{\text{app}}$ : -2.10 to +1.45 V; these data are in accordance with commonly known literature data. The capacity current in the supporting electrolyte was subtracted from the recorded currents of the electrodic processes.

A typical CVC curve for  $c_{\text{DBTMP}} = 3.3 \cdot 10^{-3}$   $\text{mol} \cdot \text{dm}^{-3}$  is given in Figure 1. It should be noted that, under conditions of our experiment, the adsorption of depolarizer molecules is possible. In the DBTMP molecule, the two bromine atoms are usually oriented towards the electrode surface, particularly

when it is positively charged; the influence of the *gauche* methyl group on the adsorption of the symmetrical bromine atoms is not known.

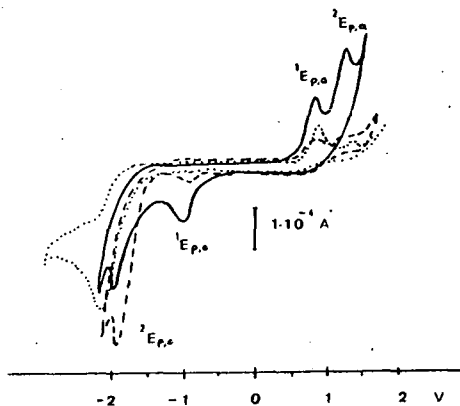
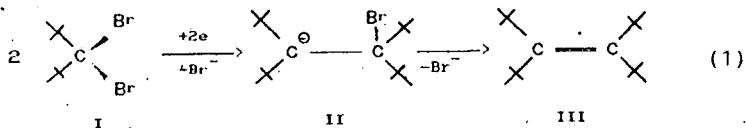


Figure 1.: Cyclic voltammograms DBTMP of  $c = 3.3 \cdot 10^{-3}$  mol dm $^{-3}$ ; reference electrode AgCl (KCl $_{\text{sat}}$  H $_2$ O), Ag: supporting electrolyte Bu $_4$ N $^+$ ClO $_4^-$  (0.1 mol dm $^{-3}$ )  $v = 0.1$  Vs $^{-1}$ ; in DMF. GCE: ... Pt $_{\text{pol}}$ : - - - - ; Au $_{\text{app}}$ : — .

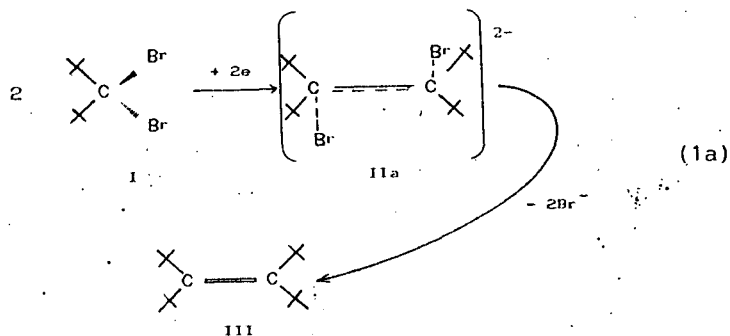
With selected ranges of the polarization potentials, the electroreduction and electrooxidation processes were found to be independent of one another and the of the nature of the electrode.

(i) *Electroreduction processes*

The most desirable product of the electroreduction of DBTMP would be tetra-tert-butylethylene, sought in both chemical [22] and electrochemical [2] processes. The mechanism of such a reaction could be as in equations (1) and (1a):

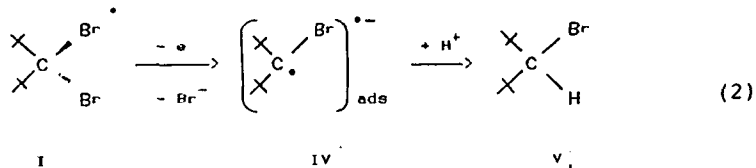


OR:



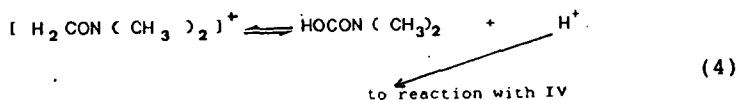
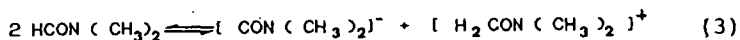
Our experiment revealed another mechanism of the electroreduction process. On the GCE electrode (Fig. 1), a single-stage process of reduction at the potential  ${}^2E_{p,c} = -1.95$  to  $-2.00$  V is visible. On the Pt<sub>pol</sub> electrode, a small peak with  ${}^1E_{p,c} = -0.95$  to  $-1.00$  V appears. At the same potential values on the Au<sub>app</sub> electrode peak currents  ${}^1I_{p,c} \approx {}^2I_{p,c}$ , clearly indicating the two-stage process of DBTMP electroreduction.

Electrolysis at a potential  ${}^1E_{p,c} = -0.95$  V leads to the formation of 2,2,4,4-tetramethylpentane monobromine according to Equation (2):



This result, which differs from expectations, may be explained as follows:

1. The sterically differentiated methyl groups (A and B) cause the adsorption of Br oriented towards the electrode. It may be assumed that the *gauche* methyl group B has a decisive influence on this process.
2. According to the known electrode properties, activated Pt and Au electrodes catalyse the process of electroreduction of Br with the formation of anion radical IV (Equation 2).
3. Anion radical IV generated on the electrode is a strong base, which acquires a proton after shift of the autodissociation equilibrium of DMF [23]:

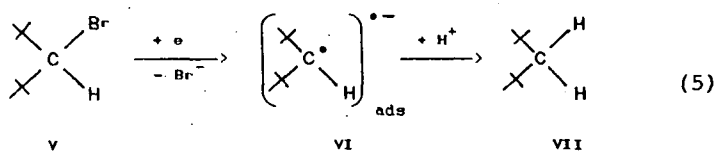


After the flow of equivalent charge  $\approx 1 \text{ F} \cdot \text{mol}^{-1}$ , peaks a and b (Fig. 2) are of similar heights.

Additional confirmation of the suggested mechanism of the reaction may be negative result of the analogous attempt



in acetonitrile.



In the next stage of electroreduction, at the potential  ${}^2E_{p,c} = -2.00$  V monobromide v is reduced to 2,2,4,4-tetramethylpentane.

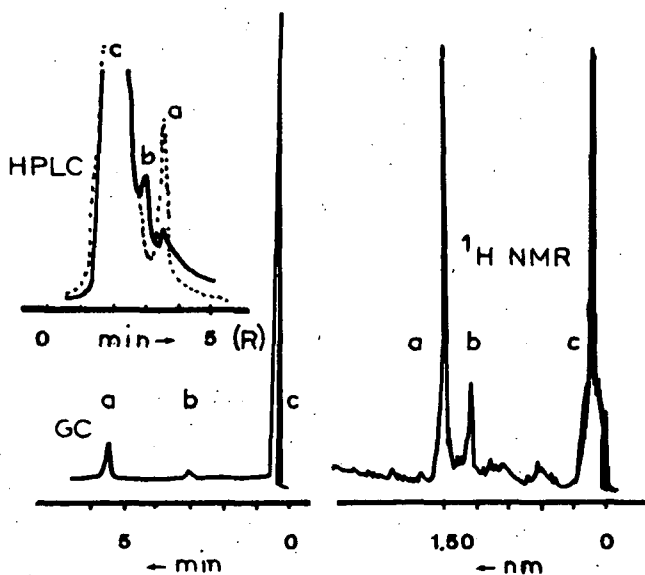


Figure 2.: Spectral analysis of products of electroreduction reactions: a - 3,3'-dibromo-2,2,4,4-tetramethylpentane; b - 3-bromo-2,2,4,4-tetramethylpentane; c - DMF and supporting electrolyte.

Peak a (Fig. 2) vanishes in favour peak b after the flow of the equivalent charge  $2 F \cdot \text{mol}^{-1}$ . Thus the mechanism of the second stage of the electroreduction may be suggested to be as in equation (5).

(ii) *Electrooxidation processes*

In the anodic branch of the polarization curve, the electrooxidation of DBTMP also exhibits two stages (Fig.1). The processes are characterized by the following peak currents: a clearly flattened peak with potential

${}^1E_{p,a} = +0.90$  to  $+1.10$  V, and a sharp peak with potential

${}^2E_{p,a} = +1.35$  V.

Similarly as in the above-described examinations of the electroreduction processes, CPE was conducted at  ${}^1E_{p,a}$  and  ${}^2E_{p,a}$ .

The charges used were  $1.22$  and  $0.82 F \text{ mol}^{-1}$ . The HPLC, GC and  ${}^1\text{H}$  NMR analysis demonstrated the loss of peaks a (Fig. 2) without the appearance of new spectra characteristic of other linking. Thus, it may be assumed that strongly ionized products are formed in the solution, whose spectra are similar to those of the solvent and supporting electrolyte (peaks c in Fig.2).

Extraction attempts with a typical non-polar solvent (n-pentane) did not reveal the reaction products in the liquid phase. It is obvious that, after the addition of water to precipitate  $\text{Bu}_4\text{N}^+\text{ClO}_4^-$ , the hydrolysis always led to 2.2.4.4-tetramethylpentanol.

Examinations of the compounds of the type tetra-tert-butyl-tetrahydrene [24, 25] have shown electron transfer is hindered by steric barriers, and ion radicals may be formed under the conditions of anodic oxidation. This was concluded because cation radicals observed with ESR methods were

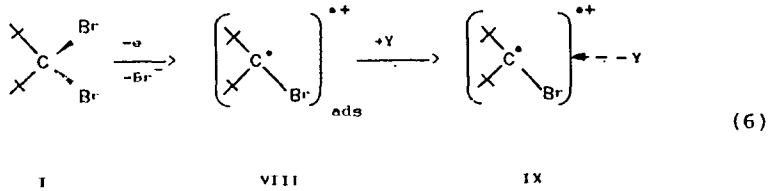
identical with the cation radicals generated by means of classical chemical oxidation. Those reactions are catalysed under the appropriate Lewis' acid-base conditions, and the products are captured in the special "traps". In this case, the parallel observations by means of spectral methods (e.g. *in situ* CVC-ESR) or freezing of the reaction products were used. These methods were also used in the work of Fox et al. [24]. The information that CVC was performed at 203 K in their work does not seem to be very reliable, because of the melting point of acetonitrile (232 K).

The CVC curves recorded at 253 K are more reliable [25]. In this way, many cation radicals of type  $R^{\cdot+}$  were isolated from the group of tetra-tert-butyl compounds. Their structures were determined by using MNDO-UMF or MNDO-RHF methods [25, 26].

Thus, the process carried out by means of CVC methods even at the sweep potential polarization rate to  $10 \text{ Vs}^{-1}$  in the oscilloscopic observation of curves and CPE at 298 K is an extremely fast reaction. The transformation to other forms of the generated compounds is also possible. Such reasoning is to be found in the earlier work of Miller [26] where, for a similar group of compounds on a platinum electrode at 0.6 V, a signal impossible to interpretation was obtained.

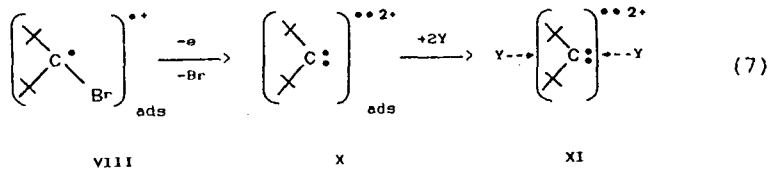
Thus, since the products of DBTMP electrooxidation give spectra in the same range as the "background", the mechanism of the anodic oxidation of DBTMP may be suggested only as probable. To a first approximation, the mechanism of the electrochemical processes taking place at a potential

$^1E_{p,a} = +0.90 \text{ V}$  is:

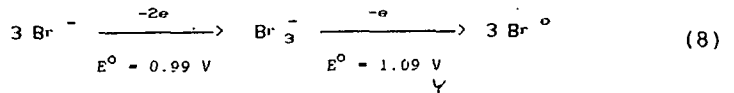


where  $Y = \text{DMF}$  or  $\text{ClO}_4^-$

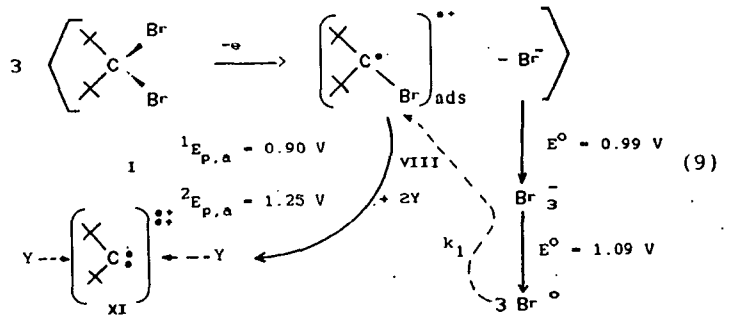
and then at a potential  ${}^2E_{p,a} = +1.35 \text{ V}$ :



The broad peak at  ${}^1E_{p,a}$  and the literature data [13] indicate the possibility of the existence of the parallel process in the potential range  ${}^1E_{p,a}$  to  ${}^2E_{p,a} = +0.90$  to  $+1.35 \text{ V}$ . This process involves the oxidation of  $\text{Br}^-$  ion and the consequent appearance of a new chemical oxidizer [13]:



The existence of such a process was proved by analysis of Nicholson and Shain [19, 20]. On this basis, the mechanism of the anodic oxidation of DBTMP suggested in Equations (6) and (7) is as follows:



The cation radicals of type XI formed are solvated in the reaction environment or they form ionpairs with the anions of the supporting electrolyte.

### *Conclusions*

The preparative processes of controlled potential electrolysis do not promise great success in this group of sterically stressed geminal compounds. On the other hand, the use of generated radicals of types VII and XI as mediators of the chemical oxidation of the other organic compounds in homogeneous emulsions seems to be very interesting.

### *Acknowledgements*

The authors are grateful to Prof. G. Maier and Dr. E. Röcker of the Institut für Organische Chemie, Justus Liebig Universität Giesse (BRD), for providing DBTMP and making possible certain experimental examinations. We thank Prof. Mihály Novák of the Institute of Physical Chemistry, JATE University, Szeged, for helpful discussions.

The investigation was conducted with the partial support of grant CPBP 01.15/4.08

## References

- [1] Kalinowski, H.O., E. Röcker, G. Maier: *Org. Magn. Res.*, 21, 64 (1983).
- [2] Fry, A.J.: in *Synthetic Organic Electrochemistry*, Wesley, Univ. Harper and Row Publ. (1972) pp. 178-187.
- [3] Ayer, W.A., L.M. Brown, S.Fung, J.B. Stothers: *Can. J. Chem.*, 54, 3272 (1976); *Org. Magn. Res.*, 1, 73 (1978).
- [4] Eliel, E.L., W.F. Bailey, L.D. Kopp, R.L. Willer, D.M. Grant, R. Bertrand, K.A. Christiansen, D.K. Dalling, M.W. Duch, E. Wenkert, F.M. Schell, D.W. Cochran: *J. Am. Chem. Soc.*, 97, 322 (1975).
- [5] Engstrom, R.C.: *Anal. Chem.*, 54 2310 (1982); *ibid.* 56, 136 (1984).
- [6] Thorton, D.C., K.T. Corby, V.A. Spendel, J. Jordan, A. Robbat jr, D.J. Rustrom, M. Gross, G. Ritzler: *Anal. Chem.*, 57, 591 (1985).
- [7] Ravichandran, K., R.P. Baldwin: *Anal. Chem.*, 57, 1744 (1984).
- [8] Halbert, M.K., R.P. Baldwin: *Anal. Chem.*, 58, 591 (1985).
- [9] Ferro, C.M., A.J. Calandra, A.J. Arvia: *J. Electroanal. Chem.*, 55, 291 (1974).
- [10] Angell, D.M., T. Dickinson: *J. Electroanal. Chem.*, 35, 55 (1972).
- [11] Jakuszevski, B., H. Scholl: *Polish. J. Chem.*, 52, 1203 (1978); *ibid.* 53, 1855 (1979).
- [12] Romanowski, S., H. Scholl: *Elektrochim.*, 16, 1184 (1980).
- [13] Bauer, D., M. Breant: in *Electroanalytical Chemistry*, ed. A.J. Bard, M. Dekker, New York (1975) vol. 8 p. 281.
- [14] Schneider, H., H. Strehlow: *J. Electroanal. Chem.*, 12, 530 (1966).
- [15] Strehlow H.: *Electrode Potential in Non-Aqueous Solvents in Chemistry of Non-Aqueous Solvents*, ed. L. Lagowski, Acad Press, New York (1967)
- [16] Parker, A.J.: *Chem. Revs.*, 69, 1, (1969).
- [17] Marcus, Y.: *Pure & Appl. Chem.*, 55, 977 (1983).
- [18] Baizer, M.M.: *Organic Electrochemistry*, M. Dekker, New York (1972).

- [19] *Nicholson, R., I. Shain: Anal. Chem., 36, 704 (1964);  
ibid. 36, 722 (1964); ibid. 37, 178 (1965).*
- [20] *Nicholson, R.: Anal. Chem., 37, 667 (1967); ibid. 37,  
135 (1967).*
- [21] *Olmstead, M., R. Nicholson: J. Electroanal. Chem., 14,  
133 (1967).*
- [22] *Buter, J., R.M. Kellog: J. Org. Chem., 42, 973 (1977).*
- [23] *Shahparonov, M.I., B. Raike, L.U. Lanshina: Fizika i  
Fizikokhimiya Zhidkosti. Khimia, Moskva (1973).*
- [24] *Fox, A.M., K.A. Campbell, S. Honig, H. Berneth,  
G. Maier, K.-A. Schneider. K.-D. Malsch: J. Org. Chem.,  
47, 3408 (1982).*
- [25] *Fox, M.A., K. Campbell, G. Maier, L.H. Franz: J. Org. Chem.,  
48, 1762 (1983).*
- [26] *Miller L.L., G.D. Norblom, E.A. Mayeda: J. Org. Chem.,  
37, 916 (1972).*

ЭЛЕКТРОДНЫЕ ПРОЦЕССЫ ПРОИЗВОДНЫХ 2,2,4,4-ТЕТРАМЕТИЛПЕНТАНА  
НА НЕПОДВИЖНЫХ ТВЕРДЫХ ЭЛЕКТРОДАХ. II. ВОЛЬТОМЕТРИЯ 3,3-  
ДИБРОМО-2,2,4,4-ТЕТРАМЕТИЛПЕНТАНА В ДИМЕТИЛФОРМАМИДЕ.

Х. Шолл, и П. Кричмоник

Изучены электродные процессы геминально замещенных 3,3'-дибромо-2,2,4,4-тетраметилпентана в ДМФ с  $0.1$  мол  $\text{дм}^{-3}$  концентрацией  $\text{Bu}_4\text{N}^+\text{ClO}_4^-$  в качестве электролита-носителя, путем циклической вольтометрии (свс) и электролиза с регулируемым потенциалом (срп) на электродах из стеклянного угля (сг), платины и золота. Продукты реакции контролировались методами жидкостной хроматографии высокого давления (нрлс), газо-жидкостной хроматографии (сг) и ядерного парамагнитного резонанса (1н-нмр).

В результате двухстадийных процессов электродного восстановления  $^1E_{p,c} = -1.00$  в и  $^2E_{p,c} = -2.00$  в  $\text{AgCl}(\text{KCl}_{\text{sat}}, \text{H}_2\text{O})\text{Ag}$ , образовались соответственно монобромид и алифатические соединения.

Сложные процессы электроокислации ( $E > +1.00\text{в}$ ), вероятно ведут к образованию катион-радикалов  $\text{BTMP}^+$  и  $\text{TMP}^{2+}$  сильно сольватированных в ДМФ, или образующих ионные пары с соответствующими анионами электролита-носителя.