ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 5, pp. 1001–1003. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.Sh. Kagan, V.V. Yanilkin, V.I. Morozov, N.V. Nastapova, I.Yu. Zhukova, I.I. Kashparov, V.P. Kashparova, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 5, pp. 829–831.

Mechanism of Electrochemical Oxidation of 1-Chloro-2,2,6,6-tetramethylpiperidine

E. Sh. Kagan[a], V. V. Yanilkin[b], V. I. Morozov[b], N. V. Nastapova[b], I. Yu. Zhukova[a], I. I. Kashparov[a], and V. P. Kashparova[a]

[a] *South-Russian State Technical University (Novocherkassk Polytechnical Institute), ul. Prosveshcheniya 132, Novocherkassk, 346421 Russia*
e-mail: kagan29@mail.ru

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, ul. Arbuzova 8, Kazan, 420088 Tatarstan, Russia*
e-mail: yan@iopc.knc.ru

Received December 4, 2009

Abstract—In contrast to 2,2,6,6-tetramethylpiperidine and other aliphatic amines, at the electrochemical oxidation of 1-chloro-2,2,6,6-tetramethylpiperidine a sufficiently stable cation-radical is formed. Its formation is confirmed by the data of cyclic voltammetry and electron paramagnetic resonance. Further transformation of the cation-radical leads to the formation of 2,2,6,6-tetramethylpiperidin-1-oxyl.

DOI: 10.1134/S1070363209050235

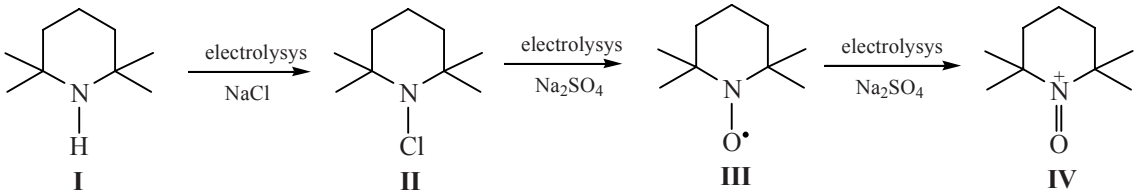
Earlier [1] we showed that electrolysis of 2,2,6,6-tetramethylpiperidine (**I**) in the presence of chloride ions in a diaphragmless elecrolyzer in a two-phase system methylene chloride–water afforded the respective nitroxyl radical, 2,2,6,6-tetramethylpiperidin-1-oxyl (**III**) (Scheme 1). The same nitroxyl radical is formed also at the electrolysis under similar conditions of 1-chloro-2,2,6,6-tetramethylpiperidine (**II**, Scheme 1). However, mechanism of this reaction remained unclear. Scheme 1 shows an oxidation of 2,2,6,6-tetramethylpiperidine **I** into nitroxyl radical **III** and oxoammonium salt **IV** via 1-chloro-2,2,6,6-tetramethylpiperidine **II**.

Preparative synthesis of radical **III** can also be performed by oxidation on anode in an electrolyzer with a diaphragm-separated cells using compound **I** as an initial substance (Scheme 1). At the electrolyzis with the diaphragm-type electrolyzer, in the organic phase remains unreacted **II**, while water phase contains oxoammonium salt **IV**. No other product was detected in the water phase. For the isolation of the reaction products the oxoammonium salt **IV** was reduced with sodium nitrite or sodium hydroxide into the respective nitroxyl radical **III** which was readily soluble in organic solvents and could be easily recovered from the water phase.

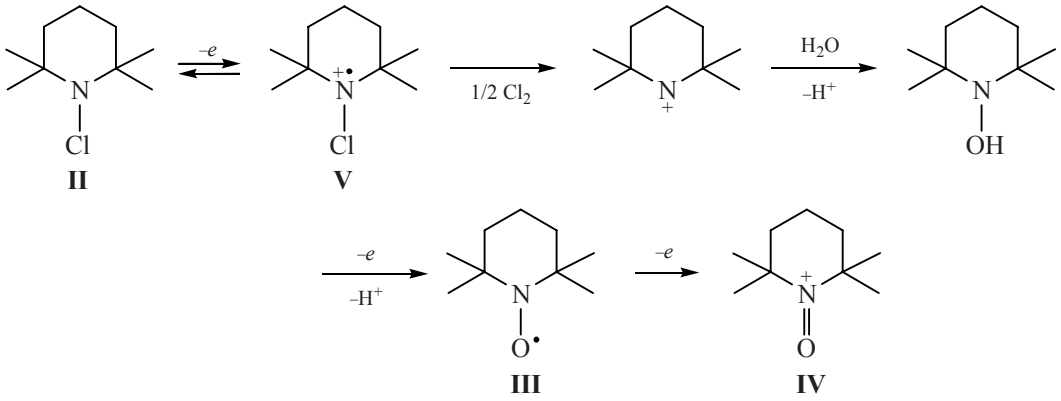
The result obtained probably means that in a diaphragmless electrolyzer the nitroxyl radical **III** is formed in the process of chloroamine **II** oxidation.

It is suggested [2–4] that in the first step of oxidation of amines a single electron transfer occurs and the respective cation-radical is formed, despite the fact that in the majority of cases the cation-radicals have not been identified owing to their short life-time,

Scheme 1.



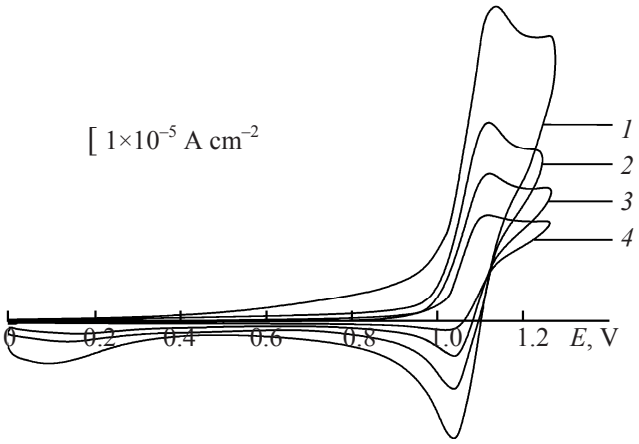
Scheme 2.



and their formation has been presumed from the character of the formed final products.

In contrast to 2,2,6,6-tetramethylpiperidine and to the majority of the other aliphatic amines, the electrochemical oxidation of **II** (Scheme 2) in acetonitrile afforded a rather stable cation-radical **V** (the half-life time at 243 K is ~10 min), whose existence was evidenced by the cyclic voltammetry (CVA) and ESR spectroscopy. Scheme 2 shows the assumed mechanism of formation of nitroxyl radical **III** and oxoammonium salt **IV**.

On the CVA curves of chloroamine **II** at the temperature 22°C an oxidation peak is fixed at +1.10 V (relatively to Ag/0.01 M $AgNO_3$ in MeCN) and its conjugated peak of re-reduction at +1.04 V (see figure). The difference in the peaks potential ΔE_p = 60 mV is typical of the reversible one-electron process [5] and evidences the formation of the primary cation-radical **V**. In the time scale of registration of CVA curves (seconds) the cation-radicals enter chemical reactions that is indicated by the decrease in the relative height of the re-reduction peak at the diminished potential sweep rate. One of the reaction products is molecular chlorine whose shallow reduction peak is registered at the potential +0.10 V.



Cyclic voltammogram curves of 1-chloro-2,2,6,6-tetramethylpiperidine (**I**) (c 3×10^{-3} M) on a glass carbon electrode in the CH_3CN/0.1 M Bu_4NBF_4 medium at varied potential sweep rates, V s^{-1}: (*1*) 0.2 ; (*2*) 0.1; (*3*) 0.05; and (*4*) 0.02.

We also succeeded to register the cation-radicals **V** and identify them by ESR spectroscopy by carrying out electrooxidation of **II** on a Pt electrode in an ampoule directly in the resonator of the ESR spectrometer at low temperature (243 K). The spectrum of cation-radical **V** consists of 12 peaks with the following characteristics: g = 2.0093, a_N = 2.11 mT, a_{Cl}^{35} = 0.6 mT, a_{Cl}^{37} = 0.5 mT.

Proceeding from the data obtained, we describe the process of formation of nitroxyl radical **III** and oxoammonium ion **IV** at the oxidation of chloroamin **II** by Scheme 2 that includes the steps of formation of cation-radical **V**, elimination of chlorine molecule followed by hydroxylation, elimination of protons and electron transfer.

EXPERIMENTAL

2,2,6,6-Tetramethylpiperidin-1-oxyl from 1-chloro-2,2,6,6-tetramethylpiperidine. The synthesis was carried out in a diaphragm type electrolyzer of 150 ml capacity. For the anode and cathode were used platinum plates of the area 20 cm^2 and 10 cm^2 respectively. To the electrolyzer anode cell was placed 7.1 g (0.05 mol) of sodium sulfate dissolved in 80 ml

of a buffer solution (0.05 M Na_2HPO_4 and 0.05 M KH_2PO_4; pH 6.86), and 3.5 g (0.02 mol) of 1-chloro-2,2,6,6-tetramethylpiperidine in 30 ml of methylene chloride. To the catode cell was loaded 40 ml of 10 % sodium sulfate solution.

The electrolysis was carried out at the current power 1.5 A (current density 0.075 A cm^{-2}). The synthesis was stopped after passing 4 F of electricity. The organic layer was separated from the water phase. To the water layer was added 10% sodium hydroxide solution to pH 10–11 and the product was extracted with methylene chloride (3×30 ml). Organic extracts were combined, the solvent was distilled off, and residue was purified by sublimation in a vacuum (10–15 mm Hg). Finally 0.65 g of compound **III** was obtained, mp 35–36°C, yield 82% on the reacted compound **II**. From organic layer the solvent was removed in a rotory evaporator and the residue was distilled in a vacuum, fraction 61–63°C (7 mm Hg) was collected and 1.74 g of 1-chloro-2,2,6,6-tetramethylpiperidine was recovered.

REFERENCES

1. Kashparova, V.P., Vlasova, E.V., Zhukova, I.Yu., Kagan, E.Sh., and Il'chibaeva, I.B., *Elektrokhimiya*, 2007, vol. 43, no. 10, p. 1.
2. Chow, Y.L., Danen, W.C., Nelsen, S.F., and Rosenblatt, D.N., *Chem. Rev*., 1978, vol. 78, no. 3, p. 243.
3. Randall, S., Deinhammer, Ho, M., Anderegg, J.W., and Porter, M.D., *Langmuir*, 1994, no. 10, p. 1306.
4. Yip, R.W., Vidoczy, T., Snyder, R.W., and Chow, Y.L., *J. Phys. Chem*., 1978, vol. 82, no. 10, p. 1194.
5. Esida, K., *Elektrookislenie v organicheskoi khimii. Rol' kation-radikalov kak itermediatov v sinteze* (Electrooxidation in Organic Chemistry. Cation-Radicals as Intermediates in the Synthesis), Beletskaya, I.P., Ed., Moscow: Mir, 1987.