Mendeleev Communications

Mendeleev Commun., 2025, **35**, 417–419

Electrochemical behavior of bridged 1,2,4-dioxazolidine derivative in acetonitrile medium on the smooth gold

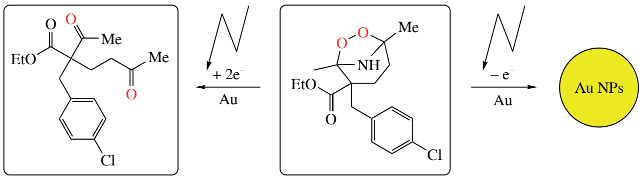
Mikhail V. Polyakov,*[a] Marina D. Vedenyapina,[a] Alexander M. Skundin,[b] Ivan A. Yaremenko,[a] Peter S. Radulov[a] and Yulia Yu. Belyakova[a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: Satpolyak@yandex.ru*

[b] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119071 Moscow, Russian Federation*

DOI: 10.71267/mencom.7714

Bridged bicyclic peroxide with 1,2,4-dioxazolidine core, namely, ethyl 2-(4-chlorobenzyl)-1,5-dimethyl-6,7-dioxa-8-azabicyclo[3.2.1]octane-2-carboxylate, was studied by cyclic voltammetry in acetonitrile medium on a smooth gold electrode. During the cathode process, two electrons are transferred, with the first electron transfer being reversible; a mechanism of cathode reduction of the substrate involves acetonitrile as the source of protons. The anodic oxidation involves the formation of colloidal gold particles due to corrosion of the gold electrode.



Keywords: cyclic voltammetry, cathodic reduction, anodic oxidation, gold, peroxides, 1,2,4-dioxazolidines, 6,7-dioxa-8-azabicyclo-[3.2.1]octane.

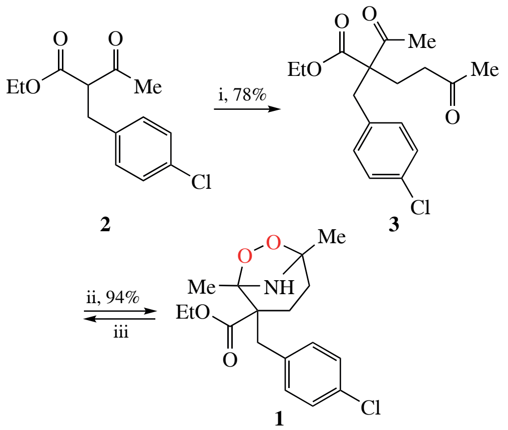
Organic peroxides are widely used in organic synthesis[1] and as industrial initiators of radical polymerization.[2] Various organic peroxides exhibit anticancer,[3,4] antiprotozoal,[5,6] anthelmintic,[5] fungicidal[7,8] and antimalarial[4,9–11] activities. Electrochemical methods are most suitable for studying redox properties of cyclic peroxides.[12–19] Studies using the cyclic voltammetry method make it possible to determine the potentials of electrode processes and the number of electrons involved in the cleavage of the peroxide bond and, therefore, to establish the mechanism of electrochemical reaction.[12–16,20]

Previously, high reducing ability of gold electrodes toward peroxide compounds was established, both in aqueous[12,13,21] and acetonitrile[22,23] media. Also, peroxide compounds were found to contribute to the dissolution of the gold anode into the acetonitrile medium with the formation of colloidal particles of gold.[22,23]

In this work, in order to establish the effect of the additional amino group on the stability of the peroxide bond and on the potential for its reduction, we chose bicyclic amino peroxide **1**, ethyl 2-(4-chlorobenzyl)-1,5-dimethyl-6,7-dioxa-8-azabicyclo-[3.2.1]octane-2-carboxylate, as the substrate. Compound **1** was obtained in two steps from ethyl 2-(4-chlorobenzyl)-3-oxobutanoate **2** (Scheme 1) using the reported method.[7,24] The Michael reaction of CH acid **2** with methyl vinyl ketone gave adduct **3** which was then oxidized with H_2O_2 in the presence of NH_4OAc to form the 6,7-dioxa-8-azabicyclo[3.2.1]octane framework.

When gold electrode was immersed into the studied solution of compound **1** in acetonitrile, a steady-state potential of 0.3 V was established relative to the silver chloride reference electrode, after which the cyclic voltammogram (CV) was recorded. Figure 1 shows the CVs for the gold electrode in the solution of compound **1** in the potential range *E* from 300 to –2800 mV, at different potential scan rates *ν* from 200 to 500 mV s^{-1}. Two peaks are observed on the cathode branch of the CVs. The first one is reversible and is located in the potential range from –600 to –1300 mV; the second peak is irreversible and is located in the potential range from –1600 to –2700 mV.

For the CVs of compound **1** recorded on gold electrode, a salient feature was found that distinguishes it from other peroxides studied previously.[13,22,23] This was the presence of a quasi-reversible peak for the first stage of reduction is observed on the anodic branch of scanning of the cathodic region in the potential range from –900 to –300 mV (see Figure 1). The difference between the potentials of the reduction and oxidation peaks is varying from 200 to 300 mV depending on the



Scheme 1 *Reagents and conditions*: i, MeC(O)CH=CH$_2$, CeCl$_3$·7H$_2$O, NaI, room temperature; ii, H_2O_2 (35% aq.), NH$_4$OAc, MeOH, room temperature; iii, Au cathode, Pt anode, Bu$_4$NBF$_4$, MeCN, *I* = 2 mA.

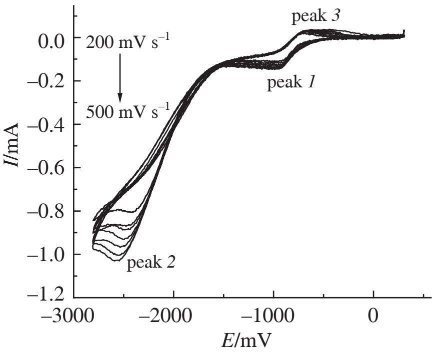


Figure 1 Cyclic voltammograms of MeCN solution of amino peroxide **1** in the cathode region on the Au-electrode, ν = 200, 250, 300, 350, 400, 450, 500 mV s^{-1}.

potential scan rate (the gap increases with increasing scan rate).

Linear dependences I_c^p–$\nu^{0.5}$ for the peaks in the cathode region of the CVs were established (see Online Supplementary Materials, Figure S1), so all processes in the studied ranges of potentials are limited by the stage of diffusion when transporting the substrate to the surface of the electrode.[25,26] The coefficients of electron transfer (α) and diffusion coefficients (D) were calculated taking into account the slopes of these linear dependences for each process (Table 1).

Some difference is noticeable in the orders of values of the diffusion coefficients. The lowest value of D is observed for the process occurring with the neutral species **1**, further processes occurring with the intermediate (that formed after the transfer of the first electron) have higher values of the diffusion coefficient D, *i.e.* the process occurs at a higher rate relative to the initial process of dissociation of the O–O bond.

During the electrolysis of the solution **1** in an undivided electrochemical cell using gold cathode, the formation of diketone **3** for chemical synthesis was detected by NMR spectroscopy (see Scheme 1). A similar electroreduction process was recorded in our previous work[23] concerning the electrochemical behavior of a similar ozonide, which differs from **1** by the presence of bridging O atom instead of NH grouping. It is obvious that the reduction of amino peroxide **1** on gold cathode occurs in a similar way as for ozonide.[23] However, we faced with an important question about the reaction mechanism, since it remained unclear how proton transfer to the radical anion intermediates formed during the cleavage of the O–O bond is possible in acetonitrile medium in the absence of good proton donors. In a system containing only amino peroxide **1** or ozonide, acetonitrile and a quaternary ammonium salt, no obvious candidates being proton sources are seen. Therefore, it looks necessary to understand who is the real proton donor.

Table 1 Calculated parameters for cathode peaks.

Peak	αn_a	$\frac{dI}{d\nu^{0.5}}$ /A s$^{0.5}$ V$^{-0.5}$	D/cm^2 s^{-1}
1	0.50	-1.21×10^{-4}	1.57×10^{-7}
2	0.35	-2.58×10^{-4}	1.02×10^{-6}
3	0.40	9.21×10^{-4}	1.13×10^{-5}

The literature provides examples of acetonitrile being proton sources under the influence of an electric current,[27] which initiates the formation of C-centered anions that act as a strong bases to deprotonate acetonitrile.[27] The processes of formation of C-centered radicals and anions from Bu$_4$NBF$_4$ are described for platinum[28] and glassy carbon electrodes;[29] if such anion is formed from acetonitrile, it is capable of further dimerization[27] and trimerization.[30] Apparently, similar processes can also occur on a gold electrode in the presence of organic peroxides, since after the cleavage of the O–O bond, both C-centered radicals and C-centered anions can form, which would subsequently subtract a proton from acetonitrile. Based on that hypothesis, we present the following possible mechanism for the electroreduction of amino peroxide **1** in acetonitrile medium on a gold cathode (Scheme 2).

After recording the CVs on a gold disk electrode in the potential range E from 400 to 2800 mV, reproducible CVs were obtained [Figure 2(*a*)]. The anodic peak was recorded in the potential range from 1400 to 2800 mV. A quasi-reversible peak of reduction was also observed on the cathode branch of the anodic region of the CVs.

We have studied the electrooxidation of amino peroxide on a gold anode using the gravimetric method. As in the case of analogous ozonide,[23] we have found that the presence of compound **1** in the acetonitrile medium also promotes the

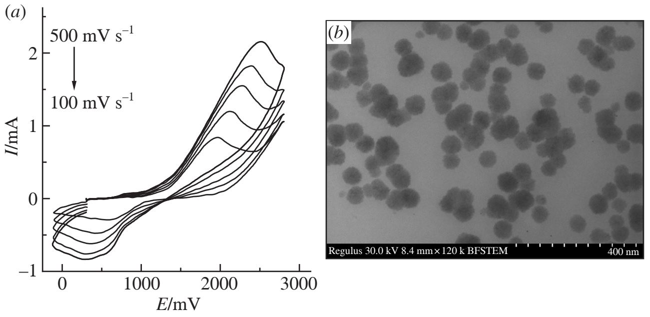
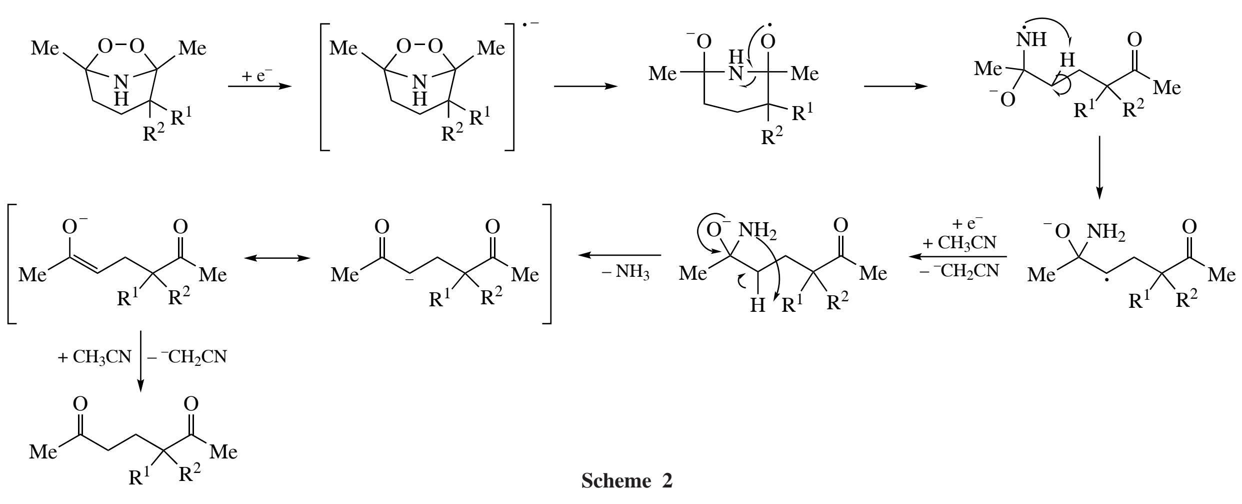
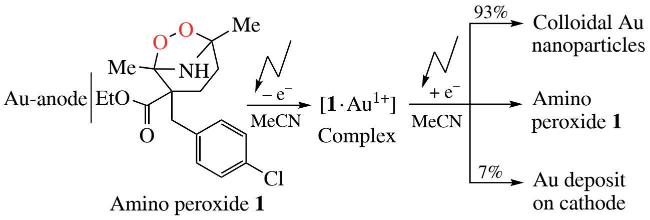


Figure 2 (*a*) Cyclic voltammograms of the solution of amino peroxide **1** in the anode region on the Au-electrode, ν = 100, 200, 300, 400, 500 mV s^{-1}. (*b*) TEM image of Au nanoparticles.



Scheme 2



Scheme 3

dissolution of the gold anode. During the entire experiment (8.5 h), the weight of the gold anode decreased by 4.1 mg, and the weight of the cathode increased by 0.3 mg. We assume that the mechanism of the anodic corrosion of the gold electrode should not differ from the one we presented in the earlier article[23] (Scheme 3).

The presence of gold particles in the solution was confirmed by X-ray fluorescence analysis. The images of gold nanoparticles were obtained using transmission electron microscopy [Figure 2(*b*)]. The colloidal particles formed have a size of 40–80 nm.

To conclude, the electrochemical behavior of bridged amino peroxide **1** of 1,2,4-dioxazolidine type on a gold electrode in an acetonitrile medium was explored. The process in the cathode region was found to occur with the transfer of two electrons, the transfer of the first electron being reversibly, expressed by the presence of a quasi-reversible peak in the CVs, which was not recorded in cases of other organic peroxides. A mechanism for the electroreduction of 1,2,4-dioxazolidine on a gold cathode in an acetonitrile medium, which acts as a proton donor for C-centered anions, is proposed. The gravimetric method showed that the corrosion of the gold electrode occurs in the anodic space with the formation of gold nanoparticles, and the transfer of gold particles to the cathode proceeds in a small extent.

The work was supported by ongoing institutional funding at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences (project no. FFZZ-2022-03). No additional grants to carry out or direct this particular research were obtained. The authors are grateful to the Department of Structural Studies of Zelinsky Institute of Organic Chemistry, Moscow, where electron microscopy characterization was performed.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7714.

References

1 N. Kaur and D. Kishore, *Synth. Commun.*, 2014, **44**, 721; https://doi.org/10.1080/00397911.2012.746369.

2 D. Braun, *Int. J. Polym. Sci.*, 2010, 893234; https://doi.org/10.1155/2009/893234.

3 L. Herrmann, I. A. Yaremenko, A. Çapcı, J. Struwe, D. Tailor, A. Dheeraj, J. Hodek, Y. Y. Belyakova, P. S. Radulov, J. Weber, S. V. Malhotra, A. O. Terent'ev, L. Ackermann and S. B. Tsogoeva, *ChemMedChem*, 2022, **17**, e202200005; https://doi.org/10.1002/cmdc.202200005.

4 P. Coghi, I. A. Yaremenko, P. Prommana, J. N. Wu, R. L. Zhang, J. P. L. Ng, Y. Y. Belyakova, B. Y. K. Law, P. S. Radulov, C. Uthaipibull, V. K. W. Wong and A. O. Terent'ev, *ChemMedChem*, 2022, **17**, e202200328; https://doi.org/10.1002/cmdc.202200328.

5 G. Panic, U. Duthaler, B. Speich and J. Keiser, *Int. J. Parasitol.: Drugs Drug Resist.*, 2014, **4**, 185; https://doi.org/10.1016/j.ijpddr.2014.07.002.

6 K. Otoguro, M. Iwatsuki, A. Ishiyama, M. Namatame, A. Nishihara-Tukashima, H. Kiyohara, T. Hashimoto, Y. Asakawa, S. Ōmura and H. Yamada, *Phytochemistry*, 2011, **72**, 2024; https://doi.org/10.1016/j.phytochem.2011.07.015.

7 I. A. Yaremenko, P. S. Radulov, Y. Y. Belyakova, A. A. Demina, D. I. Fomenkov, D. V. Barsukov, I. R. Subbotina, F. Fleury and A. O. Terent'ev, *Chem. – Eur. J.*, 2020, **26**, 4734; https://doi.org/10.1002/chem.201904555.

8 I. A. Yaremenko, M. Y. Syromyatnikov, P. S. Radulov, Y. Y. Belyakova, D. I. Fomenkov, V. N. Popov and A. O. Terent'ev, *Molecules*, 2020, **25**, 1954; https://doi.org/10.3390/molecules25081954.

9 M. K. Tiwari and S. Chaudhary, *Med. Res. Rev.*, 2020, **40**, 1220; https://doi.org/10.1002/med.21657.

10 A. Uddin, M. Chawla, I. Irfan, S. Mahajan, S. Singh and M. Abid, *RSC Med. Chem.*, 2020, **12**, 24; https://doi.org/10.1039/d0md00244e.

11 C. M. Woodley, P. S. M. Amado, M. L. S. Cristiano and P. M. O'Neill, *Med. Res. Rev.*, 2021, **41**, 3062; https://doi.org/10.1002/med.21849.

12 M. D. Vedenyapina, A. M. Skundin, V. A. Vil', M. M. Kazakova and Y. A. Barsegyan, *Russ. J. Phys. Chem. A*, 2021, **95**, 213; https://doi.org/10.1134/S0036024421010313.

13 M. D. Vedenyapina, A. M. Skundin, V. A. Vil', M. M. Kazakova and Y. A. Barsegyan, *Russ. J. Phys. Chem. A*, 2020, **94**, 859; https://doi.org/10.1134/S0036024420040238.

14 D. C. Magri and M. S. Workentin, *Molecules*, 2014, **19**, 11999; https://doi.org/10.3390/molecules190811999.

15 D. C. Magri and M. S. Workentin, *Org. Biomol. Chem.*, 2008, **6**, 3354; https://doi.org/10.1039/b809356c.

16 D. C. Magri and M. S. Workentin, *Chemistry*, 2008, **14**, 1698; https://doi.org/10.1002/chem.200701740.

17 F. Najjar, C. André-Barrès, M. Baltas, C. Lacaze-Dufaure, D. C. Magri, M. S. Workentin and T. Tzédakis, *Chemistry*, 2007, **13**, 1174; https://doi.org/10.1002/chem.200600445.

18 B. N. Ferdousi, M. M. Islam, T. Okajima and T. Ohsaka, *Electrochim. Acta*, 2007, **53**, 968; https://doi.org/10.1016/j.electacta.2007.08.010.

19 D. C. Magri, R. L. Donkers and M. S. Workentin, *J. Photochem. Photobiol., A*, 2001, **138**, 29; https://doi.org/10.1016/S1010-6030(00)00386-5.

20 D. L. Stringle, D. C. Magri and M. S. Workentin, *Chemistry*, 2010, **16**, 178; https://doi.org/10.1002/chem.200902023.

21 M. V. Polyakov, M. D. Vedenyapina, A. M. Skundin, I. A. Yaremenko, P. S. Radulov and V. V. Kuznetsov, *Russ. J. Phys. Chem. A*, 2023, **97**, 1438; https://doi.org/10.1134/S0036024423070221.

22 M. V. Polyakov, M. D. Vedenyapina, A. M. Skundin, I. A. Yaremenko and P. S. Radulov, *Russ. Chem. Bull.*, 2024, **73**, 863; https://doi.org/10.1007/s11172-024-4200-3.

23 M. V. Polyakov, M. D. Vedenyapina, A. M. Skundin, I. A. Yaremenko and P. S. Radulov, *Russ. J. Phys. Chem. A*, 2024, **98**, 3219; https://doi.org/10.1134/S0036024424702443.

24 I. A. Yaremenko, Y. Y. Belyakova, P. S. Radulov, R. A. Novikov, M. G. Medvedev, N. V. Krivoshchapov, A. A. Korlyukov, I. V. Alabugin and A. O. Terent'ev, *J. Am. Chem. Soc.*, 2021, **143**, 6634; https://doi.org/10.1021/jacs.1c02249.

25 C. Batchelor-McAuley and R. G. Compton, *J. Electroanal. Chem.*, 2012, **669**, 73; https://doi.org/10.1016/j.jelechem.2012.01.016.

26 S. Neghmouche and T. Lanez, *Int. Lett. Chem., Phys. Astron.*, 2013, **4**, 37; https://doi.org/10.56431/p-z2dz2a.

27 I. Chiarotto, L. Mattiello and M. Feroci, *Acc. Chem. Res.*, 2019, **52**, 3297; https://doi.org/10.1021/acs.accounts.9b00465.

28 J. Simonet, Y. Astier and C. Dano, *J. Electroanal. Chem.*, 1998, **451**, 5; https://doi.org/10.1016/s0022-0728(98)00090-4.

29 C. E. Dahm and D. G. Peters, *J. Electroanal. Chem.*, 1996, **402**, 91; https://doi.org/10.1016/0022-0728(95)04209-1.

30 J. K. Foley, C. Korzeniewski and S. Pons, *Can. J. Chem.*, 1988, **66**, 201; https://doi.org/10.1139/v88-033.

Received: 19th December 2024; Com. 24/7714