ISSN 1070-4280, Russian Journal of Organic Chemistry, 2019, Vol. 55, No. 7, pp. 938–943. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Zhurnal Organicheskoi Khimii, 2019, Vol. 55, No. 7, pp. 1030–1037.

Electrochemical, Spectroscopic, and Quantum Chemical Study of Electrocatalytic Hydrogen Evolution in the Presence of *N*-Methyl-9-phenylacridinium Iodide

A. V. Dolganov[a],* **O. V. Tarasova**[a], **A. V. Balandina**[a], **O. Yu. Chernyaeva**[a], **V. Yu. Yurova**[a], **Yu. M. Selivanova**[a], and **A. D. Yudina**[a]

[a] *Ogarev Mordovian National Research State University, Saransk, Russia*
**e-mail: dolganov_sasha@mail.ru*

Received September 13, 2018; revised April 1, 2019; accepted April 12, 2019

Abstract—Main intermediates in the electrocatalytic hydrogen evolution promoted by *N*-methyl-9-phenylacridinium iodide have been identified and characterized using cyclic voltammetry (CV) and NMR and ESR spectroscopy. A probable mechanism of the process has been proposed on the basis of DFT quantum chemical calculations. Analysis of structural and energetic parameters of intermediate products has shown that the electrocatalytic process involves formation of N-protonated radical cation, followed by reductive elimination of molecular hydrogen in the bimolecular reaction of two radical cations.

Keywords: electrocatalysis, generation of hydrogen, reaction mechanism, electrochemical properties, 10-methyl-9-phenylacridinium iodide.

DOI: 10.1134/S1070428019070030

Electrolysis of water is an environmentally benign method of generation of molecular hydrogen. Water is the most accessible and almost inexhaustible source of hydrogen, and transformation of the latter back into water and electricity, which is utilized in hydrogen fuel cells, ensures environmental safety and renewability of the process [1]. Platinum is the most efficient catalyst of the hydrogen evolution reaction (HER) in acid medium, but due to high cost of platinum and its sensitivity to traces of various impurities, there is a need for catalysts based on accessible and inexpensive metals [2–13]. Most problems related to the high cost and low stability can be solved by development of metal-free molecular catalysts consisting of elements present in the atmosphere in large amounts (C, H, N, O). *N*-Methyl-9-phenylacridinium iodide (PhAcrI) is a promising candidate for the design of a family of efficient metal-free electrocatalytic systems for generation of molecular hydrogen. As shown previously, PhAcrI-based electrocatalytic hydrogen evolution systems are efficient in both aprotic solvents and in aqueous media at low pH values [14–15]. Figure 1 shows a catalytic scheme for generation of molecular hydrogen, which was proposed on the basis of electrochemical data. In order to get a deeper insight into the catalytic process and optimize the catalytic system, in this work we studied in detail the mechanism of electrocatalytic hydrogen evolution reaction and determined main intermediates using cyclic voltammetry, NMR and ESR spectroscopy, and quantum chemical calculations.

The mechanism outlined in Fig. 1 is essentially similar to the classical homolytic and heterolytic proton reduction mechanisms in the presence of transition metal-based electrocatalysts [16]. The heterolytic mechanism implies two successive electrochemical reductions of the same PhAcrI molecule with protonation of the anion (EEC path) or protonation of intermediate product (ECEC path); in both cases, the final product would be 10-methyl-9-phenyl-9,10-dihydroacridine or its protonated form.

The homolytic mechanism involves one-electron reduction of $PhAcr^+$ and subsequent protonation and bimolecular reaction between the two protonated species, which is accompanied by evolution of hydrogen.

As follows from Fig. 1, the first stage in the proposed mechanism is electrochemical reduction of acridinium ion to $PhAcr^{\cdot}$ radical which was unam-

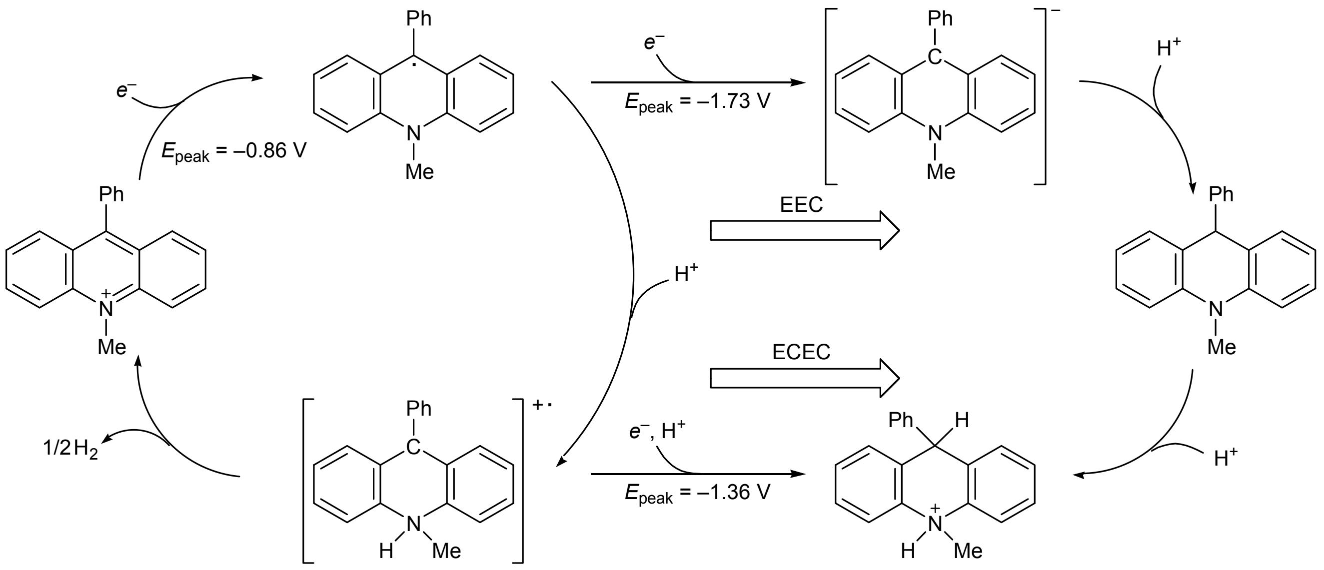


Fig. 1. Possible electrocatalytic mechanism of formation of molecular hydrogen in the presence of PhAcrI and competing EEC and ECEC mechanisms. The potentials are given relative to Fc/Fc^+ for acetonitrile solution.

biguously identified by the characteristic half-wave reduction potential (–0.86 V vs Fc/Fc^+). The potential –0.850 V corresponds to one-electron reduction of the cation to radical. Further reduction of $PhAcr^{\cdot}$ to $PhAcr^-$ is impossible at that potential, since it requires a significantly more negative potential (–1.73 V vs Fc/Fc^+). It should be noted that this process is irreversible even at high potential sweep rates (up to 10 V/s), which is likely to be related to the high reactivity of $PhAcr^-$. The anion is capable of readily abstracting a proton from the solvent (acetonitrile) molecules according to the PCET (proton-coupled electron transfer) mechanism. Taking into account that the electrochemical reaction produces a radical species, it was reasonable to consider its stability toward disproportionation leading to the initial cation and anion. If the disproportionation reaction $PhAcr^{\cdot} \rightarrow PhAcr^+ + PhAcr^-$ had taken place, the CV curve would display increase of the current of the forward reduction process and decrease of the current of the backward reaction. We found that repeated potential scan in the range from 0 to −1 V in a degassed solvent did not change the CV pattern, and the currents of both processes remained unchanged. These findings unambiguously indicate that the radical is stable in solution and that no its disproportionation occurs.

Addition of perchloric acid to a solution containing PhAcrI resulted in a considerable increase of the forward reduction current and complete disappearance of the reverse process (Fig. 2); i.e., the CV curve is typical of a homogeneous electrocatalytic process: at low acid concentration, the potential shifts to the anodic region, and increase of the acid concentration leads to cathodic shift of the potential [14].

The observed pattern corresponds to electrocatalytic reactions limited by substrate (acid) diffusion [14, 15, 17]. In the absence of PhAcrI, no reduction processes were detected in the above potential range; furthermore, no catalytic activity was observed when the spent electrode (after electrochemical studies) was placed in a fresh electrolyte solution containing no PhAcrI. This means that the electrocatalytic process is strictly homogeneous and that there is no effect of

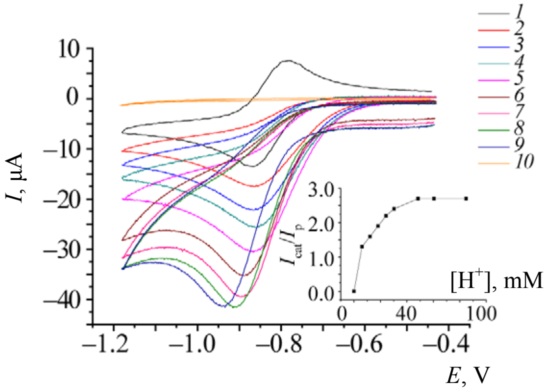
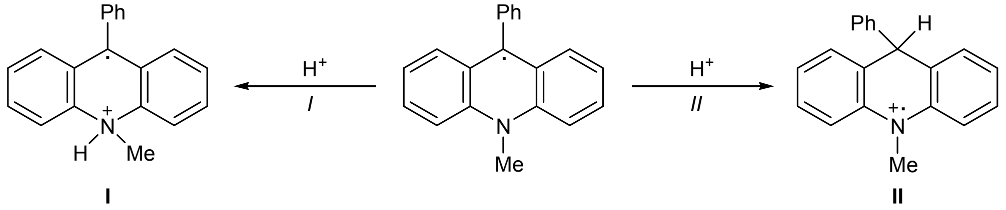


Fig. 2. (a) Cyclic voltammogram of a 1.0 mM solution of PhAcrI in acetonitrile containing (*1*) 0, (*2*) 6.05, (*3*) 12.1, (*4*) 18.15, (*5*) 24.2, (*6*) 30.25, (*7*) 48.4, (*8*) 60.5, and (*9*) 84.7 mM of $HClO_4$ and (*10*) in the absence of PhAcrI. (b) Plot of I_{cat}/I_p versus $HClO_4$ concentration (mM) at a potential sweep rate of 200 mV/s; 1.0 mM of PhAcrI in acetonitrile.

Scheme 1.



adsorption of the catalyst or its decomposition products on the electrode surface (or this effect is negligible). It should be noted that pure 10-methyl-9-phenyl-9,10-dihydroacridine showed no electrocatalytic activity at a potential of –0.850 V in the presence of 0.1 M perchloric acid; thus, EEC and ECEC mechanisms can be completely ruled out. In addition, all CV curves displayed no characteristic plateau even at a potential sweep rate of 10 V/s and high concentrations of both perchloric acid (up to 1 M) and PhAcrI (12.5 mM), indicating fast electrocatalytic process limited by substrate diffusion to the electrode surface. We can conclude that, in keeping with the proposed mechanism, the only possible second stage of the catalytic process under the given conditions is protonation of PhAcr$^{\cdot}$ at the most basic nitrogen atom with the formation of N-substituted radical cation (Scheme 1, path *I*). Interestingly, a proton could also add to the C^9 carbon atom possessing the highest electron density to form an isomeric radical cation (Scheme 1, path *II*). However, the energy of activation along path *II* is much higher than for path *I*.

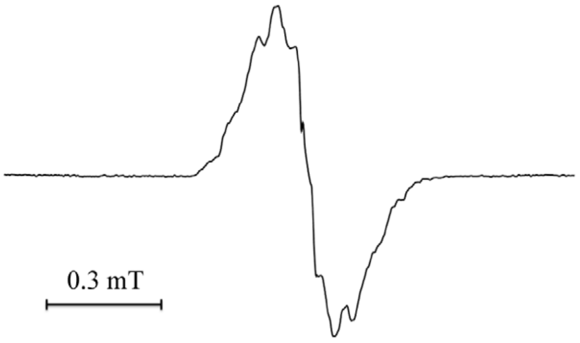


Fig. 3. ESR spectrum (X band) of a solution of PhAcr$^{\cdot}$ in benzene at room temperature.

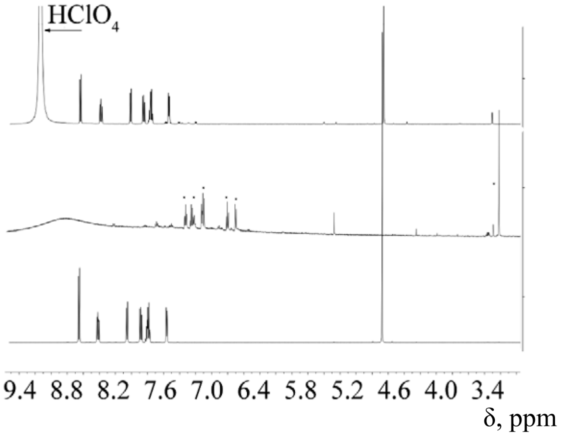


Fig. 4. ^1H NMR spectra (600 MHz) of a 3 mM solution of PhAcrI in acetonitrile-d_3 (*1*) before and (*2*) after addition of fine silver powder and (*3*) after subsequent regeneration of the initial cation by adding perchloric acid. Spectrum *2* is magnified 8 times to demonstrate broadened signals assigned to radical species. Narrow signals marked with an asterisk were assigned to the products of reversible radical dimerization on the basis of DOSY data.

In order to confirm the catalytic nature of radical species PhAcr$^{\cdot}$ and exclude all possible stages requiring the second electrochemical reduction, PhAcr$^+$ was subjected to chemical reduction with metallic silver [15, 18]. The addition of silver powder to a solution of PhAcrI in acetonitrile led to the formation of PhAcr$^{\cdot}$ radicals which were detected by ESR, NMR, and UV spectroscopy. The radicals generated in the absence of oxygen were surprisingly stable. However, the ESR spectrum of the solution (Fig. 3) was considerably broadened due to formation of noncovalent radical–radical or radical–cation dimers stabilized by π-stacking [15]. The occurrence of dynamic exchange between the radical–cation pairs also followed from the NMR spectra (Fig. 4) of a solution containing stable PhAcr$^{\cdot}$ radicals. The NMR spectra showed appreciable broadening of signals belonging to the initial cation, and these signals became narrower as the concentration of PhAcr$^{\cdot}$ decreased. After addition of an acid (a source of protons), signals belonging to the radical immediately disappeared, whereas those of initial PhAcr$^+$ appeared again (Figs. 5, 6). Furthermore, a new signal appeared in the ^1H NMR spectrum at δ 4.57 ppm (s), which was assigned to molecular hydrogen; this signal disappeared from the spectrum after purging with argon (Fig. 6). It should be noted that no chemical reaction (including formation of hydrogen) was observed when silver powder was added to an acidic solution containing no PhAcrI.

Although other catalytic paths may be proposed on the basis of the obtained data, they were excluded by the following considerations:

(1) The EEC path, which is also general for transition-metal based electrocatalysts, was ruled out because of the very negative reduction potential of PhAcr$^{\cdot}$/PhAcr^{-} (–1.73 V vs Fc/Fc^{+}); the absence of signals assignable to PhAcr^{-} in the NMR spectra of a solution of chemically generated PhAcr$^{\cdot}$ excluded formation of PhAcr^{-} as a result of disproportionation of two PhAcr$^{\cdot}$ radicals.

(2) The ECEC path, including formation of PhAcrH$^{+\cdot}$ and its subsequent reduction to PhAcrH, was ruled out since pure 10-methyl-9-phenyl-9,10-dihydroacridine (PhAcrH) showed no catalytic activity in the hydrogen evolution reaction.

The formation of radical cation **I** was detected by CV by scanning the potential in the cathodic region to –1.8 V (Fig. 7). As seen from Fig. 7, the addition of perchloric leads to the appearance of a new wave at –1.36 V (vs Fc/Fc^{+}). Most probably, the redox process PhAcrH$^{+\cdot}$ → PhAcrH occurs at that potential value, i.e., catalytically inactive species is formed. It is important that the PhAcrH$^{+\cdot}$/PhAcrH reduction wave disappears as high acid concentrations, which is very consistent with the proposed mechanism. Increase of the acidity accelerates protonation of PhAcrH$^{\cdot}$, so that the concentration of PhAcrH$^{+\cdot}$ and hence the rate of reductive elimination of hydrogen in the bimolecular reaction of two radical cations PhAcrH$^{+\cdot}$ also increase. The formation of catalytically inactive 10-methyl-9-phenyl-9,10-dihydroacridine (PhAcrH) was confirmed by preparative electrolysis of an acetonitrile solution containing PhAcrI (0.1 mM) and $HClO_4$ (0.01 M) at a redox potential of –1.36 V vs Fc/Fc^{+}. When the electrolysis was complete, the ^{1}H NMR spectrum contained signals belonging exclusively to PhAcrH. Interestingly, the amount of electricity consumed for preparative electrolysis at an acid concentration of 1 mM was larger by 28% than at an acid concentration of 0.01 M, 0.31 and 0.25 C, respectively. Thus, the preparative electrolysis data are very consistent with the data obtained by cyclic voltammetry.

The proposed mechanism was also confirmed by DFT quantum chemical calculations using B3LYP functional and 6-31+G basis set. Analysis of the vibrational frequencies showed that all assumed intermediate structures correspond to energy minima on the potential energy surface. Figure 8 shows the energy profile for the electrocatalytic formation of molecular

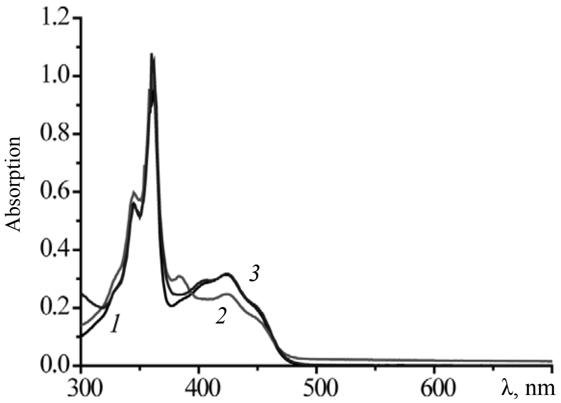


Fig. 5. UV-vis spectra of a 0.1 mM solution of PhAcrI in acetonitrile (*1*) before and (*2*) after addition of excess silver powder and (*3*) after subsequent regeneration of the initial cation by adding perchloric acid.

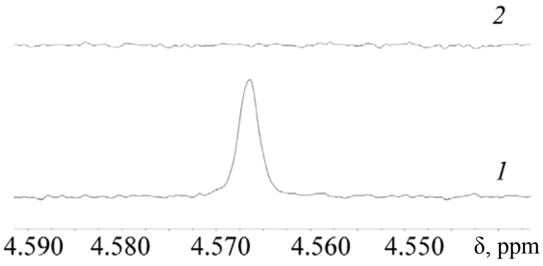


Fig. 6. ^{1}H NMR spectra (600 MHz) of a 3 mM solution of PhAcrI in acetonitrile-d_3 after (*1*) successive addition of fine silver powder and perchloric acid solution and (*2*) subsequent removal of molecular hydrogen (δ 4.565 ppm) by purging the mixture with argon.

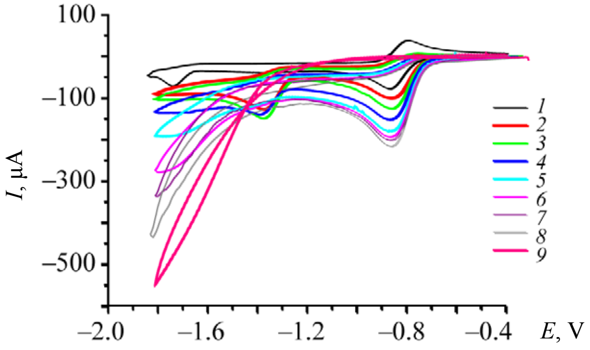


Fig. 7. Cyclic voltammograms of a 1.0 mM solution of PhAcrI in acetonitrile containing (*1*) 0, (*2*) 1.21, (*3*) 2.42, (*4*) 3.63, (*5*) 4.84, (*6*) 6.05, (*7*) 7.26, and (*8*) 8.47 mM of perchloric acid and (*9*) of a 20 mM solution of perchloric acid in acetonitrile without PhAcrI. Potential sweep rate 200 mV s^{-1}, 25°C, 0.1 M $[Bu_4N][BF_4]$ in acetonitrile, glassy carbon working electrode. The potentials are given relative to Fc/Fc^{+}.

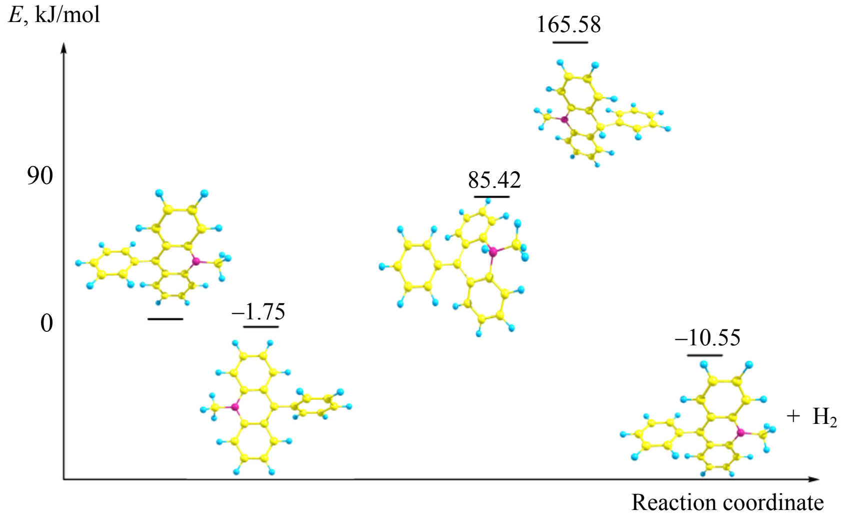


Fig. 8. Calculated energy profile of the hydrogen evolution reaction in the presence of PhAcrI.

hydrogen in the presence of PhAcrI. According to the results of calculations, the first step of the electrocatalytic process is the reduction of $PhAcr^+$ to $PhAcr^{\cdot}$. The next step is protonation of $PhAcr^{\cdot}$ at the nitrogen atom with the formation of radical cation. This step requires an energy of 87.17 kJ/mol to be overcome. This value is consistent with the energies of activation of many catalytic hydrogen evolution reactions in the presence of electrocatalytc systems based on various metal complexes and enzymes (~90 kJ/mol) [2]. Our results are very interesting. Though the energy barriers are fairly similar, catalysts of different natures (metal-free and organic metal complexes) are characterized by strongly different p*K* values. For instance, the experimental p*K* value of $PhAcrH^{+\cdot}$ in water is 4, and the complex $[(DPA\text{-}bipy)Co(OH_2)]^{n+}$ [DPA-bipy is *N*,*N*-bis(pyridin-2-ylmethyl)-2,2′-bipyridin-6-ylmethanamine which catalyzes the process with an energy of about 60 kJ/mol] has p*K* 13.9 [19]. The most probable reason is that radical cation $PhAcrH^{+\cdot}$ is unstable due to low degree of charge stabilization; stabilization of charge in metal complexes is much more effective. Therefore, we presume that hydride metal complexes formed after protonation and generally having low p*K* values are involved in the next stage (formation of molecular hydrogen) according to the heterolytic mechanism. In contrast, hydrogen elimination from radical cation $PhAcrH^{+\cdot}$ with a fairly high p*K* value is energetically more favorable according to the homolytic path since the N–H bond has a very low basicity. This assumption is well supported by the obtained data; homolytic bimolecular elimination of hydrogen requires almost three times lower energy than the heterolytic path. It should be noted that the formation of isomeric radical cation **II** (protonated at the carbon atom) requires almost twice as high energy. Our results allow us to unambiguously affirm that protonation of $PhAcr^{+\cdot}$ involves the nitrogen atom and that this reaction is the rate-limiting step. The results of calculations are consistent with the experimental data [14], according to which the rate of the catalytic process is limited by the radical protonation step.

Thus, we can convincingly conclude that the catalytic process follows the homolytic mechanism which is determined by the low basicity of radical cation formed as a result of protonation. Presumably, rational design of the molecular skeleton of acridinium cation could increase the basicity of the nitrogen atom, which should reduce the energy of formation of the radical cation and hence the rate of formation of molecular hydrogen.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-600 spectrometer (600.13 MHz for ^1H) relative to the residual proton and carbon signals of the deuterated solvent. The data were acquired and processed using Topspin 2.1 and MestReNova 9.0.0 software, respectively.

The ESR spectra were recorded on a Bruker Elexsys E500 spectrometer with the following parameters: SHF frequency 9.8 GHz, SHF power 200 mW, band width 40 G, modulation frequency 100 kHz, modulation amplitude 0.3 G, response time 200 ms, resolution 2048 points.

The electrochemical data were obtained by cyclic voltammetry in acetonitrile containing 0.1 M of tetrabutylammonium tetrafluoroborate as supporting electrolyte using a Gamry potentiostat and a 5-mL cell. The working electrode was a glassy carbon electrode with a surface area of 0.125 cm^2. The electrode was thoroughly polished and washed before measurements. A platinum electrode was used as auxiliary, and a silver chloride electrode (E^0 = 0.33 V in MeCN vs Fc/Fc^+), as reference one. All solutions were preliminarily degassed by purging argon.

10-Methyl-9-phenylacridinium iodide (PhAcrI) was synthesized by quaternization of 9-phenylacridine with methyl iodide in a hermetically closed test tube for 10 h [19]. According to the NMR data, the product contained 99.6% of the main substance. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 8.69 d (2H, 4-H, *J* = 9.2 Hz), 8.42 d.d (2H, 3-H, *J* = 9.2, 6.8 Hz), 8.04 d (2H, 1-H, *J* = 8.5 Hz), 7.94–7.83 d.d (2H, 2-H, *J* = 8.5, 6.8 Hz), 7.83–7.73 m (3H, *m*-H, *p*-H), 7.56 d (2H, *o*-H, *J* = 7.2 Hz), 4.90 s (3H, Me). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 161.65 (C^9), 141.70 (C^{12}), 138.74 (C^3), 133.32 (C^i), 130.25 (C^p), 130.18 (C^1), 129.92 (C^o), 128.89 (C^m), 127.82 (C^2), 126.21 (C^{11}), 118.68 (C^4), 39.15 (Me).

ACKNOWLEDGMENTS

The authors thank Prof. V.V. Novikov for recording the ESR and NMR spectra.

CONFLICT OF INTERESTS

No conflict of interests is declared by the authors.

REFERENCES

1. Panetier, J.A., Letko, C.S., Tilley, T.D., and Head-Gordon, M., *J. Chem. Theory Comput*., 2016, vol. 12, p. 223. doi 10.1021/acs.jctc.5b00968
2. Kaeffer, N., Chavarot-Kerlidou, M., and Artero, V., *Acc. Chem. Res*., 2015, vol. 48, p. 1286. doi 10.1021/acs.accounts.5b00058
3. Harshan, A.K., Solis, B.H., Winkler, J.R., Gray, H.B., and Hammes-Schiffer, S., *Inorg. Chem*., 2016, vol. 55, p. 2934. doi 10.1021/acs.inorgchem.5b02857
4. Anjali, B.A., Sayyed, F.B., and Suresh, C.H., *J. Phys. Chem. A*, 2016, vol. 120, p. 1112. doi 10.1021/acs.jpca.5b11543
5. Solis, B.H. and Hammes-Schiffer, S., *Inorg. Chem*., 2011, vol. 50, p. 11252. doi 10.1021/ic201842v
6. Solis, B.H. and Hammes-Schiffer, S., *Inorg. Chem*., 2014, vol. 53, p. 6427. doi 10.1021/ic5002896
7. Zarkadoulas, A., Field, M.J., Papatriantafyllopoulou, C., Fize, J., and Artero, V., *Inorg. Chem*., 2016, vol. 55, p. 432. doi 10.1021/acs.inorgchem.5b02000
8. Fogeron, T., Porcher, J.P., Gomez-Mingot, M., Todorova, T., Chamoreau, L.-M., Mellot-Draznieks, C., Li, M., and Fontecave, Y., *Dalton Trans*., 2016, vol. 45, p. 14754. doi 10.1039/C6DT01824F
9. Liao, R.Z., Wang, M., Sun, L.C., and Siegbahn, P.E.M., *Dalton Trans*., 2015, vol. 44, p. 9736. doi 10.1039/C5DT01008J
10. Dolganov, A.V., Tarasova, O.V., Moiseeva, D.N., and Muryumin, E.E., *Int. J. Hydrogen Energy*, 2016, vol. 41, p. 9312. doi 10.1016/j.ijhydene.2016.03.131
11. Dolganov, A.V., Belov, A.S., Novikov, V.V., Vologzhanina, A.V., Romanenko, G.V., Budnikova, Y.G., Zelinskii, G.E., Buzin, M.I., and Voloshin, Y.Z., *Dalton Trans*., 2015, vol. 44, p. 2476. doi 10.1039/C4DT03082F
12. Dolganov, A.V., Belaya, I.G., and Voloshin, Y.Z., *Electrochim. Acta*, 2014, vol. 125, p. 302. doi 10.1016/j.electacta.2014.01.060
13. Dolganov, A.V., Belov, A.S., Novikov, V.V., Vologzhanina, A.V., Mokhir, A., Bubnov, Y.N., and Voloshin, Y.Z., *Dalton Trans*., 2013, vol. 42, p. 4373. doi 10.1039/C3DT33073G
14. Dolganov, A., Tanaseichuk, B., Moiseeva, D., Yurova, V., Sakanyan, J., Shmelkova, N., and Lobanov, V., *Electrochem. Commun*., 2016, vol. 68, p. 59. doi 10.1016/j.elecom.2016.04.015
15. Dolganov, A.V., Tanaseichuk, B.S., Ivantsova, P.M., Tsebulaeva, Y.V., Kostrukov, S.G., Moiseeva, D.N., Shmelkova, N.M., and Yurova, V.Y., *Int. J. Electrochem. Sci*., 2016, vol. 11, p. 9559. doi 10.20964/2016.11.24
16. Artero, V. and Montecave, M., *Coord. Chem. Rev*., 2005, vol. 249, p. 1518. doi 10.1016/j.ccr.2005.01.014
17. Artero, V., Chavarot-Kerlidou, M., and Fontecave, M., *Angew. Chem., Int. Ed*., 2011, vol. 50, p. 7238. doi 10.1002/anie.201007987
18. Koper, N.W., Jonker, S.A., and Verhoeven, J.W., *Recl. Trav. Chim. Pays–Bas*, 1985, vol. 104, p. 296. doi 10.1002/recl.19851041106
19. Lewandowska-Andralojc, A., Baine, T., Zhao, X., Muckerman, J.T., Fujita, E., and Polyansky, D., *Inorg. Chem*., 2015, vol. 54, p. 4310. doi 10.1021/ic5031137