ELSEVIER
Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2014, **24**, 363–364
Mendeleev Communications

Electrooxidation of potassium hepta(methoxycarbonyl)cycloheptatrienide in acetonitrile

Vladimir A. Kokorekin,[a] Vitaliy V. Yanilkin,[b] Vladimir I. Morozov,[b] Yury V. Tomilov,[a] Dmitry N. Platonov[a] and Vladimir A. Petrosyan*[a]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: petros@ioc.ac.ru*
[b] *A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 843 275 2253; e-mail: yanilkin@iopc.ru*

DOI: 10.1016/j.mencom.2014.11.018

The quasi-reversible one-electron electrooxidation of the 1,2,3,4,5,6,7-hepta(methoxycarbonyl)cycloheptatrienide anion in MeCN at 22 °C gives a radical whose ESR spectrum consists of seven lines with splittings from six protons with an intensity ratio of 1 : 6 : 15 : 20 : 15 : 6 : 1, which likely corresponds to a substituted bicyclo[3.2.0]heptadienyl structure.

Previously, we synthesized hitherto unknown 1,2,3,4,5,6,7-hepta(methoxycarbonyl)cycloheptatriene (HMCH) and demonstrated the high stability of the HMCH$^-$ anion.[1] Studies on the reactivity of this anion and the use of polyfunctional aromatic, heterocyclic and cage structures in directed synthesis are of interest.[1–4] According to X-ray diffraction analysis, the HMCH$^-$ anion features some flattening of the seven-membered ring with elongated double bonds and shortened single bonds closest to the anionic center, which indicates a partial conjugation of five carbon atoms of the carbocycle with negative charge delocalization on the oxygen atoms of the ester groups.[1] In this case, one of the double bonds is markedly out of the plane of the five-carbon ring part, and it is not involved in the conjugated system. Owing to the presence of such a double bond, the HMCH$^-$ anion displays dual reactivity: on the one hand, being an anion, it can react as a C- or O-nucleophile with electrophiles,[1,2] and, on the other hand, having an electron-deficient double bond, it can act as a Michael acceptor and react with primary amines.[3,4]

In the light of this concept, it is of considerable interest to study the redox properties of the HMCH$^-$ anion that provides a possibility of generating and characterizing the cycloheptatrienyl radical totally substituted with ester groups. Here, we report the electrooxidation of the HMCH$^-$ anion in acetonitrile based on the data of cyclic voltammetry and microelectrolysis in the resonator of an ESR spectrometer. Previously,[5] a similar unsaturated seven-membered comparatively stable system with an unpaired electron (heptaphenyltropylium radical) was generated by the reduction of heptaphenyltropylium bromide with zinc dust in dimethoxyethane or by mixing heptaphenyltropylium bromide and potassium heptaphenylcycloheptatrienide solutions.

The starting potassium hepta(methoxycarbonyl)cycloheptatrienide (HMCH-K)[1] is well dissociated in a MeCN solution. The CV curves of this salt (C = 0.002 mol dm^{-3}, MeCN, Pt electrode and 0.1 M Bu$_4$NClO$_4$ supporting electrolyte) recorded at 22 °C contain two oxidation peaks of the anion (Figure 1).†

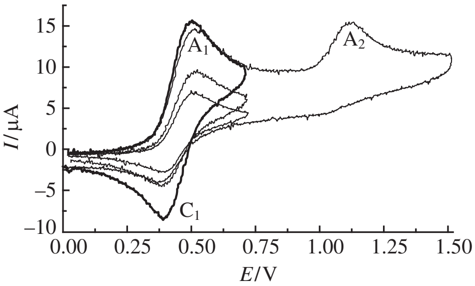


Figure 1 CV curves of HMCH-K (C = 0.002 mol dm^{-3}, v = 50, 100 and 200 mV s^{-1}) on a Pt electrode in MeCN/0.1 M Bu$_4$NClO$_4$.

Judging by the linear i_p^{1ox}–$v^{1/2}$ plot, the current of the first peak A$_1$ (E_p^{1ox} = 0.50 V) is diffusion-controlled and is approximately two times smaller than the one-electron level, as follows from a comparison with the one-electron diffusion peak of ferrocene oxidation. The rather steep shape of the A$_1$ peak is typical of reversible electron transfer, and the reverse potential scan displays a reduction peak C$_1$ (E_p^{1red} = 0.40 V) coupled with the A$_1$ peak. However, the potential difference (ΔE_p) of the A$_1$ and C$_1$ peaks at all potential scan rates was somewhat larger than the theoretical value for reversible one-electron processes. The ΔE_p value was usually 80–100 mV. A special comparison with CV of ferrocene has shown that the too high values of ΔE_p are not related to potential drop iR. Thus, it is believed that the first step of HMCH$^-$

---

† Electrooxidation of the HMCH$^-$ anion was studied by cyclic voltammetry (CV) and ESR spectroscopy combined with *in situ* electrolysis using an electrochemical cell placed in the resonator of an ESR spectrometer.[7] CV curves were recorded in an atmosphere of N$_2$ using a PI-50-1.1 potentiostat controlled by the LabView software. A platinum disc electrode (2.0 mm in diameter) sealed into glass was used as a working electrode. The electrodes were mechanically polished before measurements. A platinum wire served as an auxiliary electrode. The potentials were measured at 22 °C relative to a saturated calomel electrode (SCE). The diffusion nature of peak currents (i_p) was determined from a linear i_p–$v^{1/2}$ relationship[8] by varying the potential scan rate (v) in a range of 10–200 mV s^{-1}.

In ESR studies combined with *in situ* electrolysis (PI-50-1 potentiostat), a platinum plate served as a working electrode, a platinum wire was used as an auxiliary electrode, and a silver wire served as a reference electrode. The solutions were deaerated by repeating freezing–evacuation–thawing cycles in triplicate. The ESR spectra were recorded on an SE/X 2544 Radiopan spectrometer with an operating frequency of 9020 MHz using a quartz Dewar flask. The probe was calibrated relative to the impurity signal of the SiO$_2$ radical in quartz whose most intense component corresponds to g = 2.0002. The ESR spectra were simulated using the PEST WinSim standard program:[9] a Lorentz line shape with a width of 0.017 mT was chosen. Data were processed using Microcal Origin 6.1.

Potassium hepta(methoxycarbonyl)cycloheptatrienide (HMCH-K) was synthesized in accordance with a published procedure.[1] Commercial Bu$_4$NClO$_4$ (Acros) and acetonitrile for HPLC (Merck) were used without additional purification.

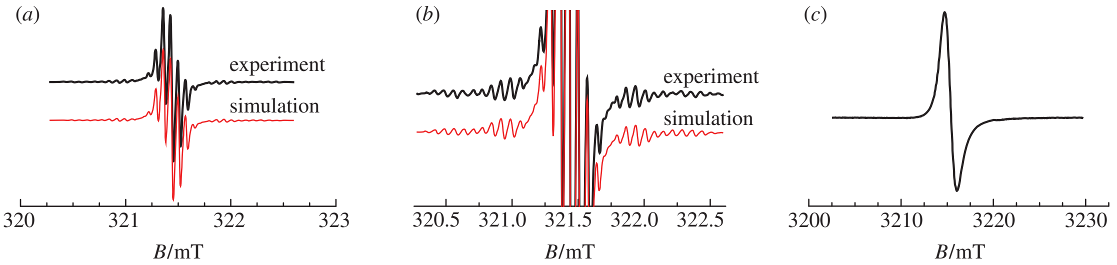


Figure 2 (*a*),(*b*) Experimental and simulated ESR spectra of HMCH$^\bullet$ radical generated by the electrochemical oxidation of HMCH-K (C = 0.002 mol dm^{-3}) at potentials of the A_1 peak on a Pt electrode in MeCN/0.1 M Bu_4NClO_4 at 22 °C and (*c*) the experimental spectrum measured at –40 °C.

anion oxidation corresponds to quasi-reversible electron transfer to give the HMCH$^\bullet$ [$C_7(CO_2Me)_7{}^\bullet$] radical.

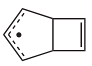
On the other hand, the height of the A_1 peak, which is smaller than the one-electron level, is inconsistent with the concept of the stability of the HMCH$^\bullet$ radical on the time scale of CV curve recording. Therefore, its formation should be confirmed by an independent experiment.

This was performed by an ESR-spectroscopic study of the microelectrolysis products (Pt anode, MeCN, 0.1 M Bu_4NClO_4) of HMCH-K. Microelectrolysis at A_1 peak potentials was carried out in an electrochemical cell placed directly in the resonator of an ESR spectrometer.

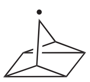
The split spectrum of a paramagnetic species with $g = 2.0034$ (Figure 2) was recorded at the A_1 oxidation peak potentials of the HMCH$^-$ anion. The intensity of this signal increased during electrolysis. The spectrum consists of seven main lines with splittings from six protons with an intensity ratio of 1 : 6 : 15 : 20 : 15 : 6 : 1. Furthermore, splittings from at least twelve ^{13}C nuclei are observed at the periphery of the spectrum [Figure 2(*b*)]. A simulation of the spectrum gives the following hyperfine coupling constants: $a_{6H} = 0.07$, $a_{1C} = 1.88$, $a_{1C} = 1.30$, $a_{2C} = 1.02$, $a_{2C} = 0.73$, $a_{2C} = 0.51$, $a_{2C} = 0.37$ and $a_{2C} = 0.26$ mT. Judging by the ESR signal intensity after electrolysis, the radical species is stable and its concentration halved at room temperature in about 4 min. At –40 °C, one broad line of another stable radical species with $g = 2.0035$ was recorded [Figure 2(*c*)], which transformed to the above split spectrum upon warming to room temperature.

It is well known[6] that, in the series of isomeric C_7H_7 radicals, such as bicyclo[3.2.0]heptadienyl **1**, 3-quadricyclanyl **2**, 7-norbornadienyl **3**, homobenzvalenyl **4** and tropyl **5**, the latter radical **5** is the most stable and the other isomeric radicals are rearranged into it. Tropyl radical $C_7(CO_2Me)_7{}^\bullet$ **5′** is the primary oxidation product of the HMCH anion detected at –40 °C. Theoretically, by analogy with radical **5** [see refs. 6(*b*),(*c*)], 22 lines with splittings from 21 equivalent protons of methyl groups can be observed for this radical. Actually, a non-split spectrum is observed in the form of a broad band, which allows the possible hyperfine coupling constant with protons to be limited to $a_{21H} \leqslant 0.008$ mT.

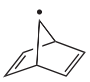
With increasing temperature, primary tropylium radical **5′** is converted into another radical whose spectrum consists of seven main lines, indicating that the unpaired electron in this radical is delocalized to a greater extent on two equivalent methoxycarbonyl groups and to a smaller extent on the others, which is typical of allylic systems.[6] We believe that the well split signal corresponds to bicyclic allylic-type radical **1′**. At 22 °C, both radicals (**5′** and **1′**) are in an equilibrium, while the broad line of tropylium radical **5′** is hidden under the split spectrum of **1′**. Accounting for the broad line considerably improves the agreement between the simulated and experimental spectra.



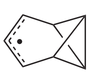
1



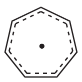
2



3

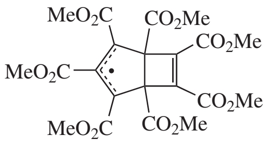


4

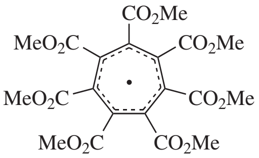


5

No examples of the transitions of tropylium radicals like **5** into isomeric radicals like **1**–**4** have been reported in the literature. This is apparently due to the very fast diffusion-controlled dimerization of radicals, whereas the isomerization of radicals occurs slowly and with a high activation energy. The presence of seven electron-withdrawing methoxycarbonyl groups in HMCH radicals hinders and slows down σ-dimerization so strongly that isomerization predominates over dimerization even at room temperature, and the formation of radicals **5′** and **1′** can be observed.



1′



5′

The next peak A_2 (E_p^{2ox} = 1.10 V) also has diffusion nature, but it is totally irreversible and its current is markedly lower than that of the A_1 peak (Figure 1). The ratio of A_1 and A_2 peak currents is nearly independent of the potential scan rate. If the potential scan direction is reversed from peak A_2, only cathodic peak C_1 is recorded. Its height is smaller than the height of this peak recorded upon reversing the potential scan direction from peak A_1. It probably means that the HMCH$^-$ oxidation product at peak A_1 potentials can be irreversibly oxidized at peak A_2 potentials.

This work was supported by the Russian Foundation for Basic Research (project nos. 12-03-00517a and 12-03-00703a).

References

1 Yu. V. Tomilov, D. N. Platonov, R. F. Salikov and G. P. Okonnishnikova, *Tetrahedron*, 2008, **64**, 10201.

2 Yu. V. Tomilov, D. N. Platonov, E. V. Shulishov and G. P. Okonnishnikova, *Tetrahedron*, 2013, **69**, 6855.

3 Yu. V. Tomilov, D. N. Platonov and G. P. Okonnishnikova, *Tetrahedron Lett.*, 2009, **50**, 5605.

4 D. N. Platonov, G. P. Okonnishnikova and Yu. V. Tomilov, *Mendeleev Commun.*, 2010, **20**, 83.

5 (*a*) M. A. Battiste, *J. Am. Chem. Soc.*, 1962, **84**, 3780; (*b*) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, 1965, **87**, 2200.

6 (*a*) F. Gerson and W. Huber, *Electron Spin Resonance Spectroscopy for Organic Radicals*, Wiley-VCH, Weinheim, 2003; (*b*) R. Sustmann, D. Brandes, F. Lanye and U. Nuchter, *Chem. Ber.*, 1985, **118**, 3500; (*c*) H.-G. Korth, W. Müller, R. Sustmann and M. Christi, *Chem. Ber.*, 1987, **120**, 1257; (*d*) R. Sustmann, D. Brandes, F. Lange and H. I. Tashtoush, *Magn. Reson. Chem.*, 1989, **27**, 340.

7 A. V. Il'yasov, Yu. M. Kargin and I. D. Morozova, *Spektry EPR organicheskikh ion-radikalov (ESR Spectra of Organic Radical Ions)*, Nauka, Moscow, 1980 (in Russian).

8 Z. Galus, *Teoreticheskie osnovy elektrokhimicheskogo analiza (Theoretical Bases of Electrochemical Analysis)*, Mir, Moscow, 1974 (in Russian).

9 D. R. Duling, *J. Magn. Reson., Ser. B*, 1994, **104**, 105.

Received: 1st April 2014; Com. 14/4338