# SYNTHESIS AND ELECTROCHEMICAL STUDY OF STABLE IMINOXYL RADICALS

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Previously we had shown that certain stable radicals can be polarographed and titrated amperometrically [1], and it was established that the value of the limiting current, found in the region of potentials ranging from +0.6 to +1.0 V (relative to the saturated calomel electrode), is proportional to the amount of iminoxyl groups in the compound. However, the behavior of iminoxyl radicals, into whose composition enter organic fragments, giving an oxidation current in the same region of potentials as the iminoxyls, remained unclear.

For this purpose we synthesized the di-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl) ester of 1,1'-ferrocenedicarboxylic acid (I) [2]. To compare the reductive capacity we used 2,2,6,6-tetramethyl-4-hydroxypiperidyl-1-oxyl (II), and also 2,2,6,6-tetramethyl-4-acetoxypiperidyl-1-oxyl (III), the di-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl) esters of suberic (IV) and azelaic (V) acids, and tri-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl-$\beta$-ethyl) phosphite (VI), whose EPR spectrum represents seven equally spaced lines (Fig. 1), which were obtained in the present paper.

Based on their oxidation current, it was established by the amperometric titration of these radicals with 0.1 N ceric sulfate solution that for monoradicals (II) and (III), and for biradicals (IV) and (V), the height of the oxidation wave corresponds respectively to one- and two-electron transitions (Figs. 2 and 3).

It is noteworthy that biradical (I) has the same height of the oxidation wave as triradical (VI), due to the oxidation of ferrocene to the ferricinium cation $[(C_5H_5)_2Fe]^+$. The one-step three-electron oxidation wave of biradical (I) testifies to the simultaneous discharge of both iminoxyl groups and the ferrocene fragment.

In order to show that the biradical (I) molecule is not degraded during electrochemical oxidation into moieties that are capable of simultaneous and separate discharge, we polarographed and amperometrically titrated a mixture of ferrocenedicarboxylic acid and radical (II) (taken in a molar ratio of 1:2). Despite the fact that also in this case the polarogram has one wave, corresponding to a three-electron transition, the solutions of this mixture when titrated, and when kept in the cold, assume an intense blue color, which is inherent to the ferricinium cation. The latter observation is found to be in agreement with the fact that ferrocene is oxidized by iminoxyl radicals. During the titration of biradical (I) the solutions remain completely colorless, which indicates that only biradical (I) is present in the solution. These data corroborate the composition of the ferrocenedicarboxylic ester (I), since its elemental analysis is difficult in view of the volatility of this compound, which is also true of many other ferrocene derivatives [3].

## EXPERIMENTAL METHOD

The polarographic studies were run on an LP-55 polarograph, while the amperometric titration was run on a AY-1 instrument, equipped with a platinum indicator electrode. The EPR spectrum was recorded on a spectrometer of the EPA-3 type.

2,2,6,6-Tetramethyl-4-acetoxypiperidyl-1-oxyl (III). To a solution of 3.4 g of 2,2,6,6-tetramethyl-4-hydroxypiperidyl-1-oxyl and 1.60 ml of absolute pyridine in 80 ml of absolute benzene was added, with

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Fig. 1

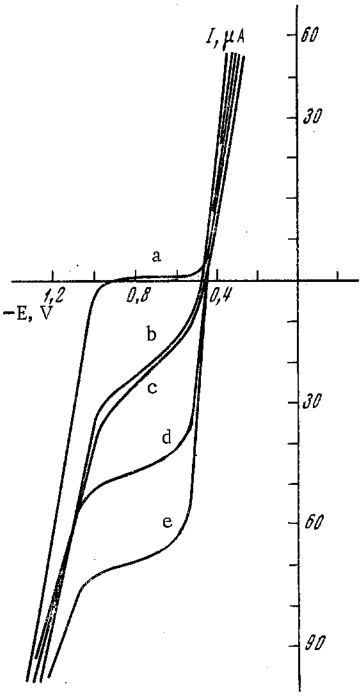

Fig. 2

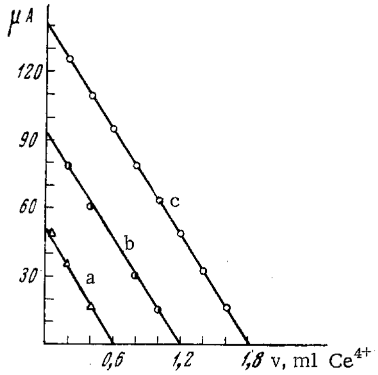

Fig. 3

Fig. 1. EPR spectrum of dilute hexane solution of triradical (VI).

Fig. 2. Oxidation polarograms of radicals in sulfuric acid aqueous acetone media: a) support; b) (II); c) (III); d) (IV); (V); e) (I), (VI).

Fig. 3. Amperometric titration curves of radicals: a) (II), (III); b) (IV), (V); c) (I), (VI).

stirring and cooling in ice water, 1.76 ml of acetyl chloride, dissolved in 40 ml of absolute benzene. The cooled reaction mixture was stirred for another 1.5 h, and then at room temperature for 10-14 h. The obtained precipitate was suction-filtered, the filtrate was evaporated, and the residue was chromatographed on a column filled with $Al_2O_3$ (II activity). Chloroform was used as the eluant. The radical forms a lower brightly colored zone, which is transferred to the filtrate. An oil is obtained after evaporation of the solvent, which crystallizes readily when allowed to stand in the refrigerator. We obtained 3.6 g (85.1%) of (III) as ruby-colored needle crystals with mp 54-55° (from hexane). Infrared spectrum ($\nu$, $cm^{-1}$): 2958 ($C-CH_3$), 2920 ($-CH_2-$), 1723 ($C=O$), 1310 ($N-O$), 1245 ($C-O$) (KBr). Found: C 61.87; H 9.88; N 6.71%. $C_{11}H_{20}O_3N$. Calculated: C 61.73; H 9.59; N 6.53%.

Di-2,2,6,6-tetramethyl-1-oxyl-4-piperidyl Ester of Suberic Acid (IV). Using the above described procedure, the compound was obtained in 72.8% yield from 8 g of 2,2,6,6-tetramethyl-4-hydroxypiperidyl-1-oxyl, 4 ml of absolute pyridine and 5.2 g of suberoyl dichloride in 80 ml of absolute benzene. (IV) was obtained as pink crystals with mp 114-115.5° (from hexane). Infrared spectrum ($\nu$, $cm^{-1}$): 2964, 2865 ($C-CH_3$), 2924 ($-CH_2-$), 1740 ($C=O$), 1338 ($N-O$), 1240 ($C-O$) (KBr). Found: C 64.71; H 9.84; N 5.96%. $C_{26}H_{46}O_2N_2$. Calculated: C 64.66; H 9.62; N 5.80%.

Di-2,2,6,6-tetramethyl-1-oxyl-4-piperidyl Ester of Azelaic Acid (V). Obtained by the above described method in 87.9% yield from 8 g of 2,2,6,6-tetramethyl-4-hydroxypiperidyl-1-oxyl, 4 ml of absolute pyridine and 5.5 g of azelaoyl dichloride in 80 ml of absolute benzene. (V) was obtained as pink crystals with mp 113-114° (from hexane). Found: C 65.27; H 9.87; N 5.61%. $C_{27}H_{48}O_6N_2$. Calculated: C 65.29; H 9.77; N 5.65%.

Di-2,2,6,6-tetramethyl-1-oxyl-4-piperidyl Ester of 1,1'-Ferrocenedicarboxylic Acid (I). Obtained in 24% yield from 1.8 g of 2,2,6,6-tetramethyl-4-hydroxypiperidyl-1-oxyl in 40 ml of absolute benzene, 1.6 ml of absolute pyridine and the dichloride of 1,1'-ferrocenedicarboxylic acid, which was prepared from 1.23 g of the acid and 0.7 ml of thionyl chloride. (I) was obtained as pink crystals with mp 98-100° (from hexane–acetone). Found: N 4.47%. $C_{30}H_{44}O_6N_2$. Calculated: N 4.79%.

Tri-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl-β-ethyl) Phosphite (VI). Obtained in a similar manner from 1.76 g of 2,2,6,6-tetramethyl-4β-hydroxyethylpiperidyl-1-oxyl, 0.9 g of triethylamine and 0.4 g of $PCl_3$ in 20 ml of absolute benzene. Phosphite (VI) was obtained as pink crystals with mp 68-69° (from hexane). Infrared spectrum ($\nu$, $cm^{-1}$): 2965 ($C-CH_3$), 2920 ($-CH_2-$), 1325 (N–O), 1050 (P–O–C). Found: N 6.62, 6.76%. $C_{33}H_{63}O_6N_3P$. Calculated: N 6.67%.

## CONCLUSIONS

1. On the example of the previously unknown free radicals, namely 2,2,6,6-tetramethyl-4-acetoxypiperidyl-1-oxyl, the di-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl) esters of suberic, azelaic and 1,1'-ferrocenedicarboxylic acids, and tri-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl-β-ethyl) phosphite, it was shown that the polarography and amperometric titration methods can be used to analyze compounds of this type.

2. Both of the iminoxyl groups and the ferrocene fragment of the di-(2,2,6,6-tetramethyl-1-oxylpiperidyl) ester of 1,1'-ferrocenedicarboxylic acid undergo a simultaneous three-electron discharge at a platinum microdisk electrode.

## LITERATURE CITED

1. A. A. Usvyatsov, V. T. Solomatin, É. G. Rozantsev, and V. A. Radionov, Data of Fourth All-Union Conference on Polarography [in Russian], Alma-Ata (1969), p. 329.
2. V. T. Solomatin and A. A. Usvyatsov, Zavodsk. Lab., 35, 778 (1969).
3. Nonbenzenoid Aromatic Compounds [Russian translation], IL (1963).