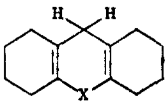
OXIDATION–REDUCTION CHARACTERISTICS OF OCTAHYDRO-CHALCOGENOXANTHENES AND OCTAHYDROXANTHYLIUM CATIONS

N. T. Berberova, A. F. Blinokhvatov, A. S. Archegova,
E. S. Klimov, A. E. Shpakov, and O. Yu. Okhlobystin

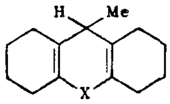
UDC 543.422.27:547.818.-9'818'814.04

Unstable radical-cations, which fragment according to the (–e, –H$^+$*, –e) scheme, are formed during the electrochemical oxidation of chalcogenooctahydroxanthenes. Free radicals (identified by ESR) are formed during the electrochemical reduction of the chalcogenooctahydroxanthylium cations.*

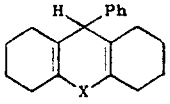
Octahydrochalcogenoxanthenes containing oxygen, sulfur, and selenium as heteroatom form a convenient model series for study of the effect of the heteroatom on the oxidation–reduction characteristics of heterocyclic compounds. In the present work we used unsubstituted sym-octahydrochalcogenoxanthenes (Ia-c), their 9-methyl (IIa-c) and 9-phenyl (IIIa-c) derivatives, and the corresponding heteroaromatic cations (IVa-c, Va-c).



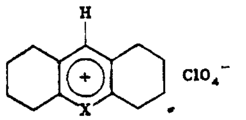
Ia-c



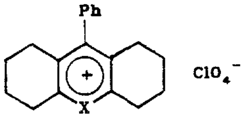
IIa-c



IIIa-c



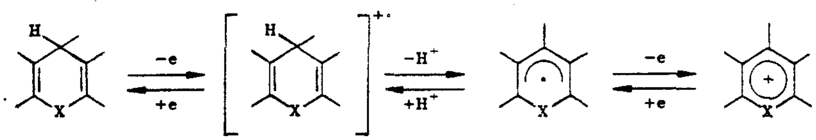
IVa-c



Va-c

I–V a X=O; b X=S; c X=Se

The one-electron oxidation of such compounds is evidently the first stage of their oxidative dehydrogenation to the corresponding heteroaromatic cations [1, 2] and is of separate interest in this respect.



Such a mechanism of dehydrogenation (–e, $-H^+$, –e), which is equivalent overall to hydride-ion "transfer," has been substantiated fairly reliably for the simplest pyrans [1] and thiopyrans [3]. It was necessary to confirm that the partially hydrogenated chalcogenoxanthenes were not exceptions. All the investigated compounds undergo electrochemical oxidation fairly readily, giving partially reversible oxidation peaks (Table 1). The oxidation rate is controlled by diffusion; a linear relationship is obtained throughout against the maximum current and the square root of the potential sweep rate as coordinates (ϑ = 0.5-100 V/sec).

In acetonitrile the number of electrons, determined with reference to a standard (ferrocene), is somewhat greater than unity. This is evidently due to the presence of traces of water in the acetonitrile. Additions of water to the electrochemical cell (up

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K. L. Khetagurov Severo-Osetinsk State University, Vladikavkaz. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 47-40, January, 1991. Original article submitted May 29, 1989; revision submitted December 4, 1989.

0009-3122/91/2701-0038$12.50

TABLE 1. Electrochemical Characteristics of Chalcogenooctahydroanthracenes (I-III)*

Compound	E_{ap}, V	E_{cp}, V	I_{cp}/I_{ap}	n
Ia	1.10	0,87	0,27	1.13
Ib	0,95	0.74	0,30	1,12
Ic	0,83	0,64	0,38	1,10
IIa	1.00	0,86	0,30	1,11
IIb	0.98	0.79	0,45	1,21
IIc	0,94	0,87	0,50	1,22
IIIa	1,18	1,06	0,34	1,13
IIIb	0.99	0.86	0,24	1,13
IIIc	0.94	0.78	0,34	1,10

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*Stationary platinum electrode, acetonitrile; E_{ap}) potential of the anodic peak, V; E_{cp}) potential of the cathodic peak, V; I) peak current, μA; n) number of electrons; θ = 0.5 V/sec

TABLE 2. First Stage of the Electrochemical Reduction of Octahydrochalcogenoxanthylium Perchlorates (IV-V) in Acetonitrile

Compound	$-E_{cp}$, V	n	$-E'_{ap}$, V	I_{ap}/I_{cp}	$+E''_{ap}$, V
IVa	0,70	1,05	0.48	0,26	0.40
IVb	0,57	1,02	0,38	0,27	0,40
IVc	0,34	1,03	0,25	0,26	0,44
Va	0,80	1,05	0,59	0,23	0,46
Vb	0,60	0.90	0.40	0,44	0,47
Vc	0,48	1,06	0.34	0,25	0,48

to 5%) lead to an increase of 1.5 times in the oxidation peak. If the acetonitrile is replaced by methylene chloride, from which the traces of water are removed more easily, the n values approximate to unity. Thus, the electrochemical oxidation of the chalcogenooctahydroanthracenes is a one-electron process and leads to the formation of unstable radical-cations.

As follows from the values of the anodic potentials of the chalcogenoxanthenes (I-III), the capacity for oxidation decreases in the series Se, S, O, and this agrees with data on the oxidation of thiopyrans [3].

The fragmentation of the radical-cations is easily traced by the electrochemical method. Thus, a reversible stage, corresponding to the formation of a proton and a xanthylium cation formed during subsequent oxidation of the free radical, is recorded on each branch of the cyclic voltammogram for all the compounds, and this is confirmed by the addition of authentic samples (Fig. 1). Exhaustive electrolysis at the oxidation potential also leads to octahydroxanthylium cations.

Oxidation of the octahydroxanthenes by lead dioxide or aluminum chloride in the resonance cavity of the ESR spectrometer leads either to unresolved ESR spectra or to spectra which cannot be interpreted unambiguously. However, the one-electron character of the chemical oxidation with 3,6-di-tert-butyl-1,2-benzoquinone is not subject to doubt. The known 3,6-di-tert-butyl-2-hydroxyphenoxyl radical was detected in the reaction of 9-phenyloctahydroselenoxanthene (IIIc) with the quinone [4]. Its formation is due to fragmentation of the initial radical-cation followed by protonation of the semiquinolate radical-anion [5].

Since the corresponding chalcogenoxanthylium cations are detected during the fragmentation of the radical-cations of the octahydrochalcogenoxanthenes, their reduction was studied separately (Table 2).

In the range of potential sweep rates between 0.5 and 100 V/sec a linear relationship is observed between the maximum current and the square root of the potential sweep rate, and this indicates that the first stage of reduction has diffusion character [6]. As follows from Table 2, the reduction wave is one-electron. (The number of electrons was determined by comparison with a one-electron standard, i.e., triphenylpyrylium perchlorate.) The I_{ap}/I_{cp} ratio on the cyclic voltammograms is significantly less than unity; the difference in the peak potentials varies between 90 and 220 mV. This indicates low reversibility for the electrochemical reduction of chalcogenoxanthyliums. On the anodic branch of the cyclic voltammogram for all the xanthylium cations, in addition to the oxidation peak of the radical, there is another light oxidation peak (0.40-0.50 V). We suppose (by analogy with [7]) that dimerization of the radical occurs. The same peaks are also formed during exhaustive electrolysis of the respective octahydrochalcogenoxanthenes.

The electroreduction of (IVa-c-Va-c) is affected both by the nature of the heteroatom and by the nature of substituent at position 9. In the series of compounds (Vc, b, a) there is an increase in the potential of the reduction peak. A similar pattern in the reduction of α-nitro derivatives of five-membered heterocycles was observed during investigation of the effect of the heteroatom on the one-electron reduction [8]. The introduction of a phenyl group for (Va-c) hinders reduction of the cations.

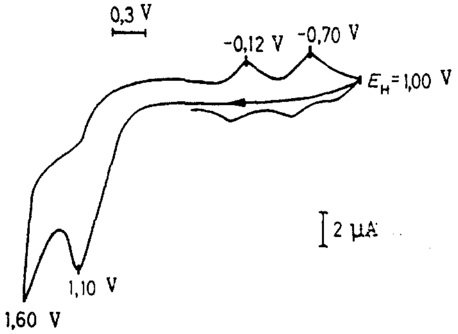

Fig. 1

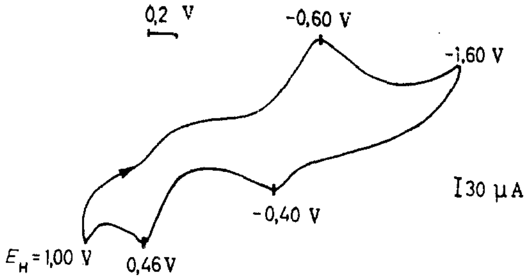

Fig. 2

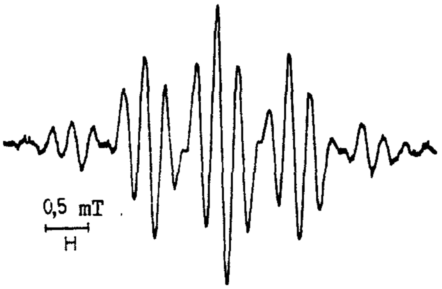

Fig. 3

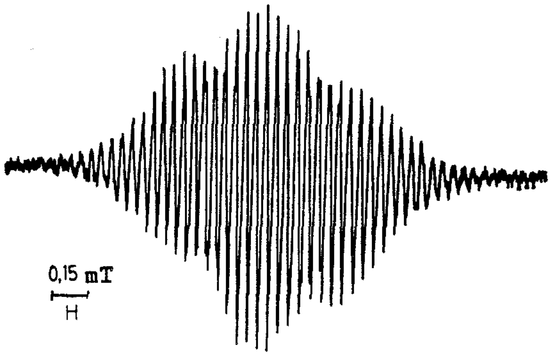

Fig. 4

Fig. 1. Cyclic voltammogram of (IIIa) (reference electrode, saturated calomel, c = $5 \cdot 10^{-3}$ M).

Fig. 2. Cyclic voltammogram of (Vb) (c = $5 \cdot 10^{-3}$ M).

Fig. 3. ESR spectrum of 9-phenyloctahydrothioxanthylium radical at 25°C.

Fig. 4. ESR spectrum of 9-phenyloctahydroxanthylium radical at 25°C.

The chemical reduction of the cations (Va, b) in the resonance cavity of the ESR spectrometer at a zinc mirror in THF leads to the appearance of signals for the corresponding neutral radicals in the ESR spectra. For (Vb) the hyperfine structure of the spectra (quintet 1:4:6:4:1 of quintets 1:4:6:4:1) is due to coupling of the unpaired electron with the four protons at positions 4, 5 ($a_H^{4,5}$ = 0.85) and 1, 8 ($a_H^{1,8}$ = 0.24 mT) of the hydrogenated rings (Fig. 3). In the case of (Va) the ESR spectrum represents a complex multiplet with a minimum splitting constant a_H = 0.04 T. The complication of the spectrum evidently arises as a result of the inclusion of the phenyl substituent in the conjugation system (Fig. 4). The weak ESR signal observed during the reduction of the cation (Vc) cannot be interpreted reliably.

EXPERIMENTAL

The ESR spectra were recorded on a Radiopan SE/X-2543 radiospectrometer under vacuum (10^{-3} mm Hg). The electrochemical measurements (CVA) were conducted with an automated PI-50-1.1 instrument (an Iskra-226 computer). The working electrode was a platinum wire with an area of $6.25 \cdot 10^{-2}$ cm^2, the reference electrode was a saturated calomel electrode with a water-impermeable diaphragm, and the auxiliary electrode was a platinum spiral. The acetonitrile was purified by distillation on a column with a total condensation head over phosphorus pentoxide (on glass wool) and then over calcium hydride. The supporting electrolyte was a 0.1 M solution of tetraethylammonium perchlorate, and the depolarizer concentration was $5 \cdot 10^{-3}$ M.

The synthesis of compounds (Ia-c, IIa, b, IIIa, b, IVa, c, Va, b) was described earlier [9-15].

9-Phenyl-sym-octahydroselenoxanthene (IIIc) ($C_{19}H_{22}Se$). To a solution of 4.15 g (25 mmoles) of methylmagnesium iodide (phenylmagnesium iodide) in 15 ml of ether we added 3.26 g (10 mmoles) of (Vc) in portions. The reaction mixture was decomposed with 2 ml of water and 13 ml of 5% hydrochloric acid and extracted with ether (3 × 20 ml). The extracts were evaporated, and 2.17 g (87%) of the colorless compound (IIIc) was obtained; mp 95-96°C (from ethanol). IR spectrum: 1634 cm^{-1} (C=C).

9-Methyl-sym-octahydroselenoxanthene (IIc) ($C_{14}H_{20}Se$). The compound was obtained similarly with a yield of 4.9 g (79.4%). The product formed colorless crystals; mp 43-44°C (from ethanol). IR spectrum: 1655, 1680 cm^{-1} (C=C).

9-Phenyl-sym-octahydroselenoxanthylium Perchlorate (Vc) ($C_{19}H_{21}ClO_4Se$). To a suspension of 1.64 g (5 mmoles) of (IIIc) in 15 ml of acetic acid we added 2.84 g (20 mmoles) of boron trifluoride etherate. The mixture was stirred for 5 h, 0.6 ml of 50% perchloric acid was added, and the mixture was diluted with 150 ml of ether. We obtained 1.9 g (88.9%) of a colorless crystalline precipitate of (Vc); mp 158-159°C (decomp.). IR spectrum: 1528 (C=C), 1100 cm^{-1} (ClO_4).

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