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FREE RADICALS AND RADICAL ANIONS IN A SERIES OF TELLUROXANTHENE DERIVATIVES

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UDC 547.818.9:542.941:543.422.27

In the one-electron reduction of telluroxanthyl or telluroxanthone perchlorates, stable 9-aryltelluroxanthyl radicals and telluroxanthone radical anion are formed. An EPR study of the distribution of spin density in such radicals gives evidence that the nature of the heteroatoms in the xanthyl fragments has an insignificant influence on the distribution of the spin density.

Stable 9-aryltelluroxanthyl radicals [1], radical cations obtained in the electrochemical oxidation of 3,4-benzo-1-tellurocyclopentane [2] and phenoxatellurine [3], and radical anions obtained generated in the electrochemical reduction of 2-nitro and 2,8-dinitrophenoxatellurines [4], have been described among the series of heterocyclic, tellurium-containing systems. However, the electrochemical characteristics and the distribution of spin density in such systems have hardly been studied at all. Besides this, they are of definite interest both for the study of the spectral characteristics of radicals with a single type of structure and for understanding the differences in reactivity of the heterocyclic compounds leading to these radicals.

The present report deals with an investigation of the reducibility of telluroxanthyl [5] and telluroxanthone systems [5, 6] by means of cyclic voltammetry and the EPR spectroscopy of the resultant radical and radical anion systems.

We obtained voltammograms of the reduction of telluroxanthyl Ib in acetonitrile. On the addition of water to the supporting electrolyte, the characteristic pair of cathodic and anodic peaks decreased to zero (Fig. 1b, c). The subsequent addition of the acid CF_3COOH to the system leads to the appearance of oxidation-reduction peaks, and the solution

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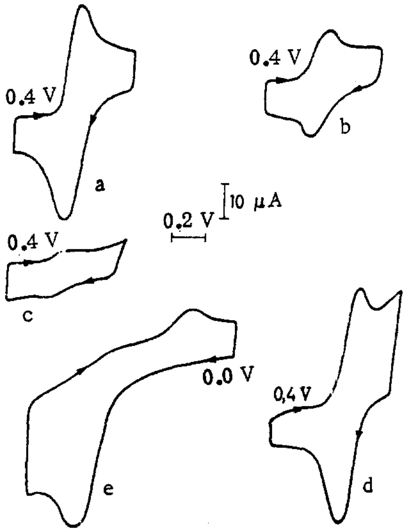
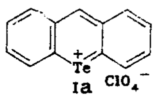
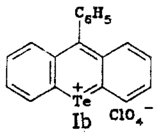


Fig. 1. Cyclic voltammograms of the reduction (a-d) and oxidation (e) of compound Ib: a) reduction of compound Ib; b) the same, 2 min after the addition of 0.05 M H_2O; c) the same, after 5 min; d) the same, after the addition of 0.25 M CF_3COOH.

TABLE 1. Characteristics of the Cyclic Voltammograms of Tellurium-Containing Heterocycles and Their Oxygen Analogs (E, potential of peak in V; I, current in μA)


Ia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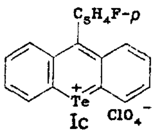
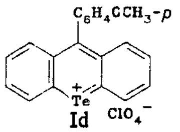
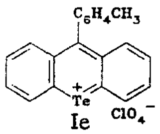
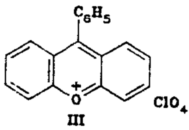
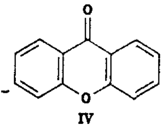
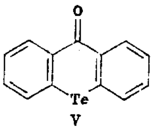

Ic

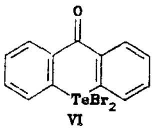

Id


Ie


III


IV

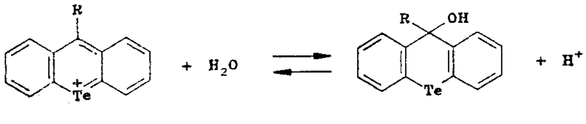

V


VI

$(C_5H_5)_2Fe$
VII

Compound	Reduction				Oxidation			
	E_{pc}	I_{pc}	E_{pa}	I_{pa}	E_{pa}	I_{pa}	E_{pc}	I_{pc}
Ia	0,02	18	0,0	7	1,10	50	0,30	—
Ib	0,06	40	0,12	39	1,04	56	0,28	8
	−0,90	18	—	—	—	—	—	—
Ic	−0,05	38	0,02	36	1,21	54	0,26	12
	−0,90	21	—	—	—	—	—	—
Id	0,03	38	0,10	40	1,21	50	0,28	10
	−0,92	20	—	—	—	—	—	—
Ie	0,01	39	0,10	40	1,14	53	0,32	8
	−1,06	28	—	—	—	—	—	—
III	−0,02	44	0,08	42	—	—	—	—
	−1,10	28	—	—	—	—	—	—
IV	−1,69	43	−1,50	41	—	—	—	—
	−2,34	40	−2,26	25	—	—	—	—
V	−1,58	37	−1,50	36	1,18	40	—	—
	−2,10	35	−2,00	20	—	—	—	—
VI	−0,36	34	—	—	1,28	64	—	—
	−1,54	38	−1,50	35	—	—	—	--
	−2,08	35	−2,01	15	—	—	—	—
VII	—	—	—	—	0,46	56	0,41	56

acquires a blue color (Fig. 1d). Obviously, the changes in the shape of the voltammograms is due to the existence of a reversible, telluroxanthyl cation-alcohol equilibrium:



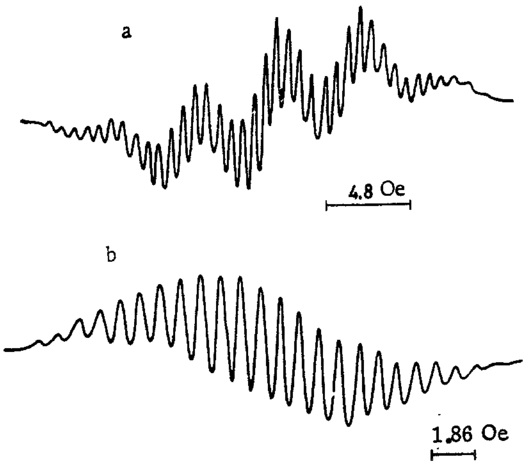
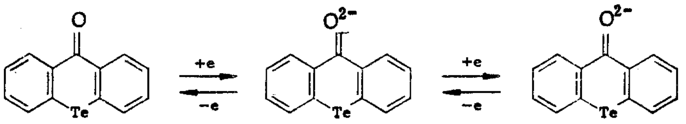


Fig. 2. EPR spectra of the phenyltelluroxanthyl radical (in THF): a) phenyltelluroxanthyl radical (10°C); b) telluroxanthone radical anion (60°C).

Data on the susceptibility of tellurium-containing heterocycles and their oxygen analogs to oxidation-reduction in dry acetonitrile are presented in Table 1. According to the potentials of the reduction peaks, compounds Ia–e have strong acceptor properties. In all the cases, the maximum current is proportional to the concentration of depolarizer and to the square root of the rate of change of the polarizing voltage. This corresponds to a diffusion-limited process [7, p. 552]. On comparing the maximum diffusion currents for the compounds studied with the reduction currents for the one-electron models IV and VII (Table 1), one can conclude that the reduction of cations Ia–e and III takes place in a one-electron step with the formation of the corresponding radicals.

The anodic (repeated) peaks on the cyclic voltammograms are equal to the cathodic, and the difference in the potentials of the peaks is close to the theoretical, therefore the electrochemical processes are completely reversible and the radical species forming are stable under the experimental conditions. Compound Ia is an exception, for which the anodic peak is smaller than the cathodic, apparently because of the subsequent dimerization reaction. A second reduction wave was observed for cations Ib–e and III; its nature was not investigated. One can surmise that it is related to the addition of a second electron with the formation of a carbanion.

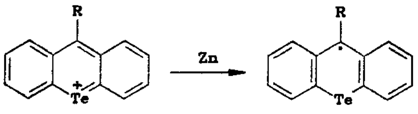
Telluroxanthone V is reduced at more negative potentials than is telluroxanthyl Ib. The reduction takes place in two steps, the first of which corresponds to the formation of the radical anion and the second, to that of the dianion, analogous to the behavior of xanthone IV in DMFA [dimethylformamide] [8].



Telluroxanthone VI, containing tetracoordinated tellurium, in the heterocycle, is, as can be seen from the potentials (Table 1, compound VII), easily reduced with the splitting off of bromine and formation of the telluroxanthone. According to the reduction potentials, telluroxanthyl Ib and telluroxanthone V (Table 1) are stronger one-electron acceptors than the analogous oxygen compounds, III and IV.

The distribution of the spin density of the unpaired electron in the stable, free radical compounds IIa–e was studied by EPR spectroscopy.

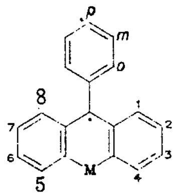
Similarly to the xanthyl [9], thioxanthyl [10], and selenoxanthyl [11] cations, the perchlorates of the telluroxanthyls, I, are readily reduced to the corresponding free radicals, II, by metallic zinc in benzene or THF.



I II

a R=H, b R=C_6H_5, c R=p-FC_6H_4, d R=p-$CH_3OC_6H_4$, e R=$C_6H_5CH_3$

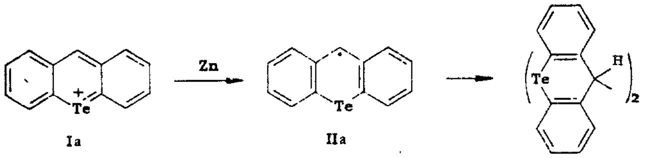
TABLE 2. Constants of the Spin Density Distribution in Radicals



M	$\alpha_1H=\alpha_8H$	$\alpha_2H=\alpha_7H$	$\alpha_3H=\alpha_6H$	$\alpha_4H=\alpha_5H$	α_oH	α_MH	α_pH	Literature
O	3,31	0,86	3,81	0,74	0,74	0,61	0,86	[9]
S	3,20	1,01	3,70	0,94	0,50	0,06	0,20	[10]
Se	3,25	1,00	3,82	1,00	0,5	0,5	0,19	[11]
Te	4,8	0,6	4,8	1,2	—	—	—	—

Data on the spin density distribution in 9-phenyltelluroxanthone radical IIb and literature data for O-, S-, and Se-containing radicals are summarized in Table 2. The EPR spectrum of radical IIb is shown in Fig. 2a. The data presented in Table 2 indicate the weak effect of the nature of the heteroatom on the spin density distribution in the xanthyl fragments of radicals of type II. The absence of HFS [hyperfine structure] in the case of the 9-phenyltelluroxanthyl radical caused by splitting on the protons of the 9-phenyl ring in the case of the 9-phenyltelluroxanthyl radical is probably due to the fact that the phenyl ring in this radical deviates from the plane of the heterocycle by a greater angle than it does in radicals containing O, S, or Se as the heteroatom. This agrees with the data in [10]. The introduction of substituents (F, CH_3OCH_3) in the para position of the 9-phenyl residue of the telluroxanthyl radical (IIb), has essentially no effect on the distribution of spin density.

Unlike the 9-aryltelluroxanthyl radicals (IIb-e) the telluroxanthyl radical (IIa, R = H) dimerizes readily and irreversibly, forming 9,9'-bis(telluroxanthenyl) [12].



The reduction of telluroxanthone on Na grains in THF leads to the formation of radical anion V, which has a well-developed HFS of the EPR spectrum (Fig. 2b). The constants of the spin density distribution in such a radical anion were determined by the EPR method:

$$\alpha_1{}^H \simeq \alpha_3{}^H \simeq \alpha_8{}^H \simeq \alpha_6{}^H \simeq 3.75\,\text{Oe},\ \alpha_2{}^H \simeq \alpha_7{}^H \simeq 1.86\,\text{Oe},\ \alpha_4{}^H \simeq \alpha_5{}^H \simeq 0.93\,\text{Oe}.$$

In contrast to the oxygen analogs, the tellurium-containing heterocycles tend to oxidize, apparently because of the strongly expressed tendency of dicoordinated tellurium derivatives to go to a higher oxidation state [14].

EXPERIMENTAL

The EPR spectra of the free radicals and radical anions were taken on an IRÉS-1001 spectrometer under strictly anaerobic conditions. The electrochemical measurements were carried out in acetonitrile with 0.1 M tetraethylammonium perchlorate as supporting electrolyte relative to a saturated calomel reference electrode. The working electrode was a platinum disk 2 mm in diameter. The concentration of the depolarizer was $5 \cdot 10^{-3}$ M. The P5827M potentiostat with a triangular pulse source was described previously [13].

The telluroxanthyl perchlorates were synthesized by the procedure in [5] and the telluroxanthone by that in [6].

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SATURATED NITROGEN-CONTAINING HETEROCYCLES.

12.* STEREOCHEMICAL PROPERTIES OF HYDROXYALKYLPYRROLIDINES USING ^{13}C NMR SPECTROSCOPY

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and I. N. Klochkova

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The ^{13}C NMR spectra of fifteen compounds in a series of alkyl- and aryl-substituted cis-isomers of hydroxyalkylpyrrolidines have been recorded, and they have been fully interpreted on the basis of configurational and conformational assignments.

We have previously reported on the synthesis of geometric isomers of 2-pyrrolidylalkanols [1-3]. By studying the ^{13}C NMR spectra of 2-hydroxyalkylpyrrolidines it was possible to identify the markedly distinctive pattern of the chemical shifts of certain nuclei, to determine the effect of substituents in the heterocycle on the chemical shifts of carbon atoms of the pyrrolidine ring and hydroxyalkyl substituent, and to study certain features of the steric structure of compounds in these series.

Assignment of the signals was carried out using a known additive method to calculate the chemical shifts of ^{13}C nuclei in substituted alkanols [4, p. 75], off-resonance data, deuteration experiments, consideration of the general characteristics for downfield shifts of carbon atoms attached to electronegative atoms, and α-, β-, and γ-effects of substituents. As a basis for calculating the shift increments of the hydroxyalkyl substituents on the pyrrolidine ring of compounds I-IV, we adopted data [4, p. 75] for unsubstituted pyrrolidine (47.1 and 25.7 ppm) and N-methylpyrrolidine (56.7 and 24.3 ppm), while for alcohols V-XV we used the experimental data for compounds I-IV (Table 1) obtained from the corresponding furan amines [5, 6].

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*For Communication 11, see [1].

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