bisector of angle O—S—O. The result obtained by Wrobel and co-workers [3] is evidently explained by the fact that the calculations of the geometrical structure were carried out using an insufficient number of starting parameters.

Thus the use of lanthanide shift reagents for the analysis of the PMR spectra of thiolene 1,1-dioxides makes it possible to simplify the spectra and to establish the preferred conformation of compounds in solution when data on the induced shifts for a sufficient number of magnetic nuclei are available.

EXPERIMENTAL

The PMR spectra of 0.2 mole/liter solutions of the substrate in $CDCl_3$ were recorded with a Tesla BS-487B spectrometer (80 MHz). The lanthanide shift reagent was introduced into the solutions in powdered form in successive portions up to a reagent/substrate molar ratio of 0.6, and the PMR spectrum was measured each time. The location of europium in the adducts was calculated with an SM-1 computer by means of the DINIYa program [6].

LITERATURE CITED

1. V. K. Boreiko et al., in: Physiologically Active Substances [in Russian], Naukova Dumka, Kiev (1983), p. 26.
2. J. T. Wrobel and K. Kabzinska, Bull. Acad. Pol. Sci., Ser. Sci. Chem., 22, 173 (1974).
3. J. T. Wrobel, K. Kabzinska, J. Ruszkowska, and P. K. Wrona, J. Mol. Struct., 41, 287 (1977).
4. T. É. Bezmenova, G. V. Klimusheva, V. I. Kulishov, S. M. Lukashev, G. G. Rodé, G. M. Soroka, and V. P. Tantsyura, Khim. Geterotsikl. Soedin., No. 8, 1056 (1977).
5. K. Kabzinska, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 29, 1 (1981).
6. M. Yu. Kornilov, A. V. Turov, and V. I. Zamkovoi, Ukr. Khim. Zh., 41, 769 (1975).
7. M. Yu. Antipin, T. É. Bezmenova, G. V. Klimusheva, G. G. Rodé, and Yu. T. Struchkov, Ukr. Fiz. Zh., 28, 553 (1983).
8. C. D. Barry, A. C. North, J. A. Glasel, and R. J. Williams, Nature, 232, 236 (1971).

ELECTROCHEMICAL MODELING OF THE OXIDATIVE DEHYDROGENATION OF 4H-THIOPYRANS

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The oxidation of substituted 4H-thiopyrans on a rotating platinum disk electrode with a ring in acetonitrile was accomplished for the first time. It was established that the dehydrogenation of both tri- and pentasubstituted thiopyrans proceeds via a scheme involving the successive transfer of an electron, a proton, and an electron (an EPE process); 4H-thiopyrans are oxidized more readily than the corresponding oxygen analogs.

Up until now, the electrochemical oxidation of 4H-thiopyrans has not been studied. In order to study the effect of a sulfur atom in the heteroring we investigated the electrochemical behavior of these compounds.

We selected 2,4,6-triphenyl- (I) and 3,5-dimethyl-2,4,6-triphenyl-4H-thiopyran (II) as the subjects of our investigation due to the fact that, as shown in [1], as a consequence of the presence of methyl substituents in the $C_{(3)}$ and $C_{(5)}$ positions of the heteroring of II, its dehydrogenation in acidic media is realized via a different mechanism than that in the dehydrogenation of thiopyran I. In analogy with other heterocyclic compounds, one might have expected that cations with both retention [2] and elimination [3] of the substituent in $C_{(4)}$ position can be formed in the electrochemical oxidation of thiopyrans I and II. We therefore initially studied the electrochemical reduction of thiopyrylium cations III-VI — possible products of the oxidation of thiopyrans I and II — on a rotating platinum disk

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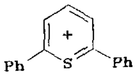
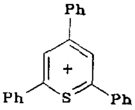
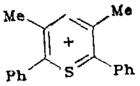
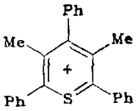
TABLE 1. Electrochemical Reduction of Thiopyrylium Cations on a Rotating Disk Electrode with a Ring in Acetonitrile*

Compound	Electrode	E^{R}_{const}, V	$E_{1/2}$, V	i_{lim}, μA	*n*	Q, %
 III	D	—	−0,20	22,2	1,0	—
	R	+0,1	—	—	—	—
 IV	D	—	−0,27	20,5	1,0	—
	R	+0,03	−0,28	2,4	—	100
 V	D	—	−0,37	21,2	1,0	—
	R	−0,07	—	—	—	—
 VI	D	—	−0,45	19,8	1,0	—
	R	−0,12	−0,47	2,0	—	85

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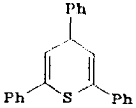
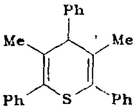
*Here and subsequently, the potentials are the values relative to an aqueous saturated calomel electrode.

TABLE 2. Results of Electrochemical Oxidation of 4H-Thiopyrans I and II on a Rotating Platinum Disk Electrode with a Ring in Acetonitrile

Compound	Electrode	E_{const}, V	$E_{1/2}$, V	i_{lim}, μA	*n*	Q, %
 I	D	—	+1,25	39,0	1,8	—
	R	$E^{R}=+0{,}7$	+1,18	0,05	—	0,5
	R	$E^{R}=-0{,}6$	+1,26	4,4	—	188
	R	$E^{D}=+1{,}5$	−0,16*	2,7	—	115
			−0,29†	2,5	—	98
 II	D	—	+1,13	36,5	1,8	—
	R	$E^{R}=+0{,}7$	—	—	—	—
	R	$E^{R}=-0{,}6$	+1,14	4,0	—	182
	R	$E^{D}=+1{,}4$	−0,16*	2,3	—	105
			−0,47†	2,7	—	113

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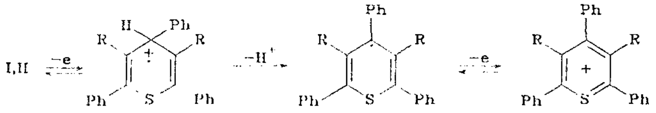
*First wave.

†Second wave.

electrode with a ring in acetonitrile. The results are presented in Table 1. It is apparent from Table 1 that cations IV and VI, which contain a phenyl substituent in the 4 position, are reduced reversibly to the corresponding radicals with the transfer of one electron; the triphenyl-substituted thiopyranyl radical, which is formed in the reduction of cation IV, is the most stable radical, as evidenced by the coefficient of the yield with respect to the current (Q, Table 1) [4]. The one-electron reduction of cations III and V is most likely accompanied by subsequent fast dimerization, since waves of oxidation of the corresponding radicals are absent when the voltammetric curves are recorded on a ring electrode. It should be noted that the investigated cations III-VI do not undergo oxidation within the limits of discharge of the inert electrolyte.

The electrochemical oxidation of thiopyrans I and II on a rotating platinum disk electrode with a ring in acetonitrile takes place in one two-electron step, and other waves are not observed up to discharge of the inert electrolyte (Table 2); in the case of thiopyran I a wave of reduction of its cation-radical is recorded on the ring (the constant potential of the ring corresponds to the foot of the wave of oxidation on the disk). The cation-radicals of thiopyran II are much less stable, and a wave of their reduction on the ring is absent. An overall wave of reduction of the cations and protons (Q, Table 2) is recorded at a constant ring potential corresponding to the beginning of the plateau of the limiting current of the reduction of cations III-VI on the ring electrode for both thiopyran I and thiopyran II. Recording of the polarization curves on a ring electrode with a constant disk potential corresponding to the beginning of the plateau of the limiting current of the oxidation of thiopyrans I and II showed that two waves are observed in both cases. The first one corresponds to reduction of the protons (−0.16 V, Table 2), and the second one corresponds to reduction of the thiopyrylium cation with a substituent in the 4 position of the heteroring (IV and VI, respectively). It follows from these results that the oxidation of thiopyrans I and II proceeds via the following scheme:



I, IV R=H; II, VI R=CH$_3$

IV, VI

The mechanism of the oxidation does not change when substituents are introduced in the 3 and 5 positions of the heteroring and is realized with the successive transfer of an electron, a proton, and an electron (an EPE process), as observed for other heterocyclic compounds [2, 5]. It should be noted that triphenyl-substituted thiopyran I is oxidized 0.16 V more readily than the corresponding oxygen analog and triphenyl-substituted thiopyrylium cation IV is reduced 0.15 V more readily than the corresponding oxygen analog [2].

EXPERIMENTAL

The conditions of the electrochemical experiment were described in [3]. The rate of revolution of the disk electrode with a ring was 2660 rpm, and the coefficient of efficiency was 0.12. The number of electrons transferred (n) was determined by comparison with the one-electron wave of the reduction of cation IV starting from the assumption that the coefficients of diffusion of the depolarizer are inversely proportional to the square root of the molecular mass. The wave of the reduction of $HClO_4$, the potential of which in acetonitrile ranges from −0.06 to −0.17 V [6], was recorded to identify the protons formed in the oxidation of the thiopyrans.

Thopyrans I and II were obtained by the methods in [7], and thiopyrylium perchlorates III-VI were prepared by the methods in [7, 8].

LITERATURE CITED

1. V. G. Kharchenko, N. I. Kozhevnikova, A. A. Shcherbakov, G. G. Aleksandrov, and Yu. T. Struchkov, Khim. Geterotsokl. Soedin., No. 3, 324 (1980).
2. N. T. Berberova, A. A. Bumber, M. V. Nekhoroshev, V. B. Panov, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 246, 108 (1979).
3. I. M. Sosonkin, G. N. Dorofeenko, G. N. Strogov, G. P. Safaryan, and A. N. Domarev, Khim. Geterotsokl. Soedin., No. 9, 1177 (1981).
4. L. N. Nekrasov, Advances in Science and Technology. Electrochemistry [in Russian], Vol. 17, All-Union Institute of Scientific and Technical Information, Moscow (1981), p. 148.
5. V. I. Shilov, O. N. Chupakhin, I. M. Sosonkin, and V. A. Subbotin, Zh. Org. Khim., 16, 202 (1980).
6. I. M. Sosonkin, G. N. Strogov, and G. L. Kalb, Élektrokhimiya, 19, 910 (1983).
7. V. G. Kharchenko, M. E. Stankevich, N. M. Kupranets, A. R. Yakoreva, V. I. Kleimenova, and S. K. Klimenko, Zh. Org. Khim., 8, 193 (1972).
8. V. G. Kharchenko, N. I. Kozhevnikova, and N. V. Voronina, Khim. Geterotsikl. Soedin., No. 4, 562 (1979).