Analytical study of five-membered heterocyclic compounds (N, S). I.
Polarographic study of 3-substituted derivatives of rhodanine

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This paper refers to the polarographic behaviour of some 3-substituted derivatives of rhodanine. The particular polarographic waves were characterized and an electrode mechanism of cathodic reduction was suggested by determination of the number of electrons exchanged, by identification of products of the potentiostatic reduction on a large mercury pool electrode, and also by ultraviolet and infrared spectroscopy. The possibility to correlate the half-wave potentials with σ values listed is pointed out.

Rhodanine (2-thio-4-thiazolidone) and its derivatives have a wide-spread use in analytical chemistry as detection reagents for some cations [1—12]. 3-Substituted derivatives of rhodanine were reported [5, 6] to be analytical reagents for Au(III), Pt(IV), Os(VIII), and Cu(II) ions determination. Also the quantitative formation of salts of rhodanine derivatives with compounds of silver was studied [7], the effects of particular groups of the thiazolidone ring were examined on appropriate model substances and the type of the reaction product formed was suggested.

So far, little attention has been paid to the electrochemical investigation of rhodanine and its derivatives. Papers dealing with the polarographic behaviour of rhodanines in both cathodic and anodic regions [13, 14] do not describe details of polarographic measurements.

Our paper refers to the polarographic behaviour of ten 3-substituted derivatives of rhodanine in Britton—Robinson buffer solutions.

Experimental

Apparatus and equipment

Polarographic waves were recorded with an LP-60 (Laboratorní přístroje, Prague) and an OH-102 (Radelkis, Budapest) polarographs. The capillary of the LP-60 polarograph had the out-flow velocity $m = 2.26$ mg s^{-1}, drop time $t_1 = 3.1$ s at the reservoir height 59 cm. The capillary of the OH-102 polarograph had the out-flow velocity $m = 2.25$ mg s^{-1}, drop time $t_1 = 3$ s and mercury level 76 cm. Kalousek polarographic vessel provided with a jacket for maintaining constant temperature had a separated mercury(I) sulfate electrode. Oxygen from the solution was removed by a stream of
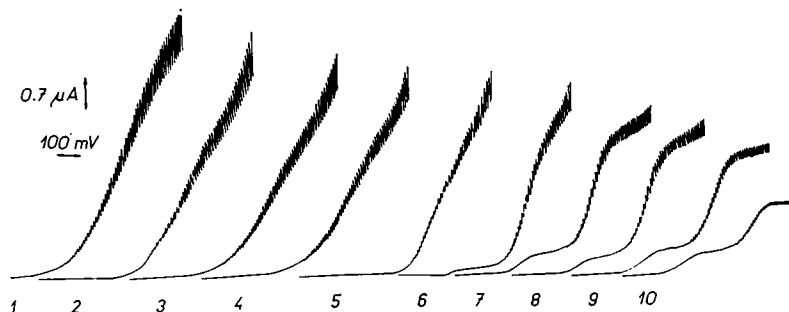
Fig. 1. Polarographic record of 3-phenylrhodanine in Britton—Robinson buffer solution in the presence of 50% methanol. The curves are recorded at 0.5 mM concentration, sensitivity 1/70 in the −1 to −3 V range. pH Values:
1. 4.25; *2.* 5.07; *3.* 5.77; *4.* 6.06; *5.* 6.38; *6.* 7.02; *7.* 7.39; *8.* 7.69; *9.* 8.85; *10.* 10.24.

bulb nitrogen purified with an alkaline solution of pyrogallol, concentrated sulfuric acid and molecular sieve Potasit 3 A. Washing bottle with 50% methanol was preset to the Kalousek vessel to avoid the loss of methanol during passing nitrogen, which lasted 5 min at a 10 cm water column pressure. The temperature was kept constant within ±0.1°C by Wobser ultrathermostat. The half-wave potentials were measured with a three-electrode system by means of a QTK compensator (Metra, Blansko) towards a saturated aqueous calomel electrode. Commutated curves were obtained by Kalousek commutator designed by the Polarographic Institute of the Czechoslovak Academy of Sciences. Electrolysis on a large mercury pool electrode was carried out at a constant potential of the limiting diffuse current by means of PRT-500-LC potentiostate (Taccussel, Lyon). The number of exchanged electrons during the electrode process was determined by a modified millicoulombpolarographic method [15—17] in a special micro vessel.

Ultraviolet spectra were taken with a UV-VIS Specord (Zeiss, Jena) spectrophotometer in the 200 to 350 nm range in 10-mm cells. Measured were 5×10^{-5} M solutions of samples in spectral methanol. Infrared spectra were recorded with an M-225 (Perkin—Elmer) spectrophotometer in the 400 to 4000 cm^{-1} range using KBr technique.

The pH values were estimated with an OP-205 (Radelkis, Budapest) pH-meter.

Chemicals

All chemicals employed were of anal. grade (Lachema, Brno) and were used directly with the exception of tetramethylammonium iodide (TMAI), which was twice crystallized from distilled water and dried *in vacuo*. Freshly distilled diethyl ether was used for extraction of the products of electrolysis.
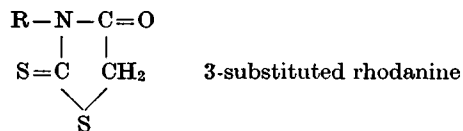
Derivatives under investigation were prepared according to [18]. Their purity was checked spectrophotometrically, by elemental analysis and melting point. Characteristic data of products thus prepared are listed in Table 1.

Results and discussion

The polarographic behaviour of the prepared substances was investigated in various supporting electrolytes. No significant difference in the course of polarographic waves

Table 1

Characteristic data of synthesized rhodanines

$$R-N-C=O$$
$$S=C \quad CH_2 \quad \text{3-substituted rhodanine}$$
$$S$$

No.	R	Formula	M	Calculated/found		Yield [%]	M.p. or b.p. [°C corrected]	
				% S	% N		Found	Reported
I	Phenyl	$C_9H_7NOS_2$	209.295	30.64	6.7	38.6	192—194	192—193
				30.73	6.71			
II	p-Tolyl	$C_{10}H_9NCS_2$	223.322	28.71	6.27	72.6	166.5—168	168.5—169.5
				—	—			
III	p-Ethoxyphenyl	$C_{11}H_{11}NO_2S_2$	253.349	25.31	5.53	50.8	185—189	180—188
				—	—			
IV	p-Bromophenyl	$C_9H_6BrNOS_2$	288.203	22.25	4.86	67.1	162—163	162—162.5
				22.30	4.88			
V	p-Methoxyphenyl	$C_{10}H_9NO_2S_2$	239.322	26.80	5.85	55.3	153.5—154	155.5—156
VI	p-Dimethylaminophenyl	$C_{11}H_{12}N_2OS_2$	252.365	25.41	10.7	45.5	204—206*	—
				25.84	10.96			
VII	p-Nitrophenyl	$C_9H_8N_2O_3S_2$	254.295	25.22	11.02	21.0	226—228*	229—230*
				—	—			
VIII	p-Carbethoxyphenyl	$C_{12}H_{11}NO_3S_2$	281.360	22.79	4.97	54.2	114—115	—
				23.07	5.12			
IX	p-Acetylphenyl	$C_{11}H_9NO_2S_2$	251.333	25.52	5.57	50.2	146—147	147—148
				—	—			
X	m-Acetaminophenyl	$C_{11}H_{10}N_2O_2S_2$	266.349	24.07	10.51	46.5	220—222*	—
				23.60	10.19			

* Melting point with decomposition.

was observed and therefore only results obtained in the universal Britton—Robinson buffer solution in the presence of 50% methanol are given. This concentration was considered optimal basing upon preliminary tests of solubility of substances under study in dilute methanol, even though polarographic measurements indicated a decrease of limiting current with the increase of concentration of methanol.

All fundamental measurements were done with a 0.5 mM solution of 3-phenylrhodanine or 3-(p-tolyl)rhodanine within pH 4.25 to 11.505 range. The investigated derivatives did not reveal a cathodic wave under pH 4.25. In the given pH range rhodanines disclose two anodic and two cathodic waves. The anodic waves are well pronounced and could be measured in a broad pH region. The anodic waves have, as we have evidenced by investigation of current criteria, an adsorption character.

Anodic waves of substances with an incorporated thio grouping were studied [19—23]; it has been found that a reaction of mono- or bivalent mercury with sulfur is involved. Waves corresponding to a one-electron transfer are assigned following reaction scheme

$$R-S + H^+ \rightarrow R-S-H^+,$$

$$2R-SH^+ + 2Hg \rightarrow Hg_2(R-S-H)_2 + 2e,$$

$$2R-SH^+ + Hg \rightarrow Hg(R-S-H)_2 + 2e.$$
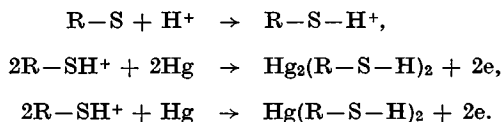
When comparing the anodic waves of the 3-substituted derivatives of rhodanine under study with the mentioned opinions, one can deduce that the suggested scheme is correct, this being proved mainly by the dependence of $E_{1/2}$ anodic waves upon pH; this dependence indicates the participation of hydrogen ions in the reaction. The anodic to cathodic current ratio was found to be 1 : 2; this evidences that the anodic wave is one-electron wave, since in cathodic reduction two electrons are exchanged as it will be shown later.

In the pH 4.25 to 7.4 range 3-substituted rhodanines exhibit only one cathodic wave (i_{c2}), as seen in Fig. 1. The $E_{1/2}$ value of this wave increases linearly with pH up to 6.45 (Fig. 2). Above this pH the $E_{1/2}$ value is pH independent. The pH rise to alkaline region resulted in formation of a new cathodic wave (i_{c1}), the $E_{1/2}$ of which is by 300 mV more positive. The $E_{1/2}$ was virtually constant up to pH 8.85, then it increased linearly. The
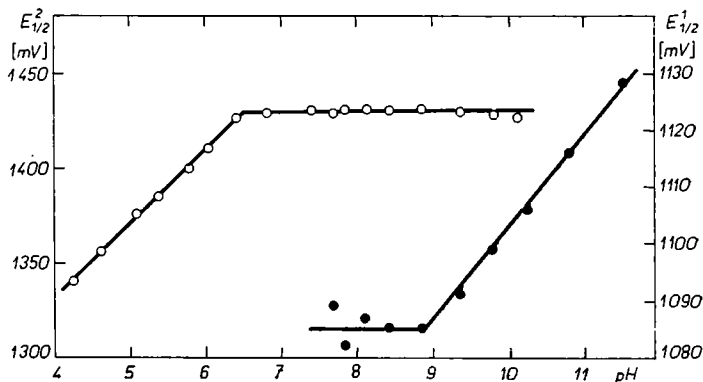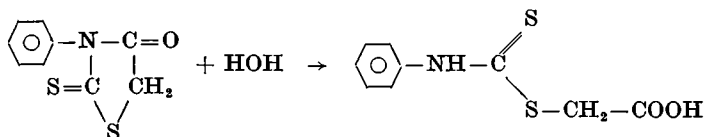

Fig. 2. Dependence of $E_{1/2}$ on pH of cathodic reduction of 3-phenylrhodanine.
○ i_{c1} first wave; ● i_{c2} second wave

generation of this cathodic wave in the pH 7.45 to 8.85 range can be due to the reduction of N-phenylthiocarbamoylmercaptoacetic acid formed as a result of decyclization of the rhodanine ring according to following reaction

$$\langle O \rangle - N - C = O \quad + HOH \quad \rightarrow \quad \langle O \rangle - NH - C \Big\langle {}^{S}_{S - CH_2 - COOH}$$

Above the pH 8.85 a total hydrolysis took place yielding the corresponding phenyl isothiocyanate (PITC) and thioglycolic acid. The i_{c2} wave corresponded, in the alkaline medium above pH 8.85, to the reduction of the PITC formed, this being evidenced by the $E_{1/2}$ value measured with an original PITC (Table 2).

The data of polarographic currents measured proved the cathodic waves to be of diffuse character. The reduction process proceeded irreversibly as indicated by measurements employing Kalousek commutator. The number of exchanged electrons could not be therefore determined by logarithmic analysis, but millicoulombpolarographically; the ascertained values corresponded to two electrons per one molecule.

Whether reduction of the carbonyl or thione group took place it was evidenced by isolation of products of potentiostatic electroreduction over a large mercury pool elec-

Table 2

Values of $E_{1/2}$ dependence of 3-phenylrhodanine on pH in Britton—Robinson buffer solution

pH	$E_{1/2}$ [mV]			
	i_{a1}	i_{a2}	i_{c1}	i_{c2}
4.25	+52	−197		−1340
4.60	+35	−230		−1355
5.075	+10	−248		−1373
5.37	+3	−253		−1384.5
5.77	−30	−295		−1399
6.06	−52	−310		−1409
6.38	−74	−336		−1426
6.85	−90	−350		−1427
7.23	−128	−369		−1429
7.39	−140	−405		−1430
7.69	−152	−410	−1089	−1429
7.84	−168	−454	−1082	−1428
8.13	−180	−460	−1087	−1429
8.43	−195	−461	−1085	−1429
8.85			−1085	−1430
9.37			−1091	−1429
9.79			−1099	−1427
10.24			−1106	−1425
10.78			−1116	
11.505			−1128	
11.505			−1120.5*	

* Refer to PITC.

Table 3

$E_{1/2}$ and σ values for 3-substituted derivatives of rhodanine

No.	3-Substituted derivatives	$E_{1/2}$ [mV]		σ	Remark
		B—R pH 6.85	0.05 M TMAI		
1	Phenyl	−1427	−1420	0	
2	p-Tolyl	−1440	−1427	−0.17	
3	p-Bromophenyl	−1415	−1407	0.23	
4	p-Ethoxyphenyl	−1451	−1438	−0.25	
5	p-Methoxyphenyl	−1445	−1439	−0.26	
6	p-Dimethylaminophenyl	−1388	−1390	−0.20	
7	p-Nitrophenyl	−1380	−1366	0.78	$E_{1/2}$ of NO$_2$ is −417 mV
8	p-Carbethoxyphenyl	−1383	−1381	0.52	
9	p-Acetylphenyl	−1395 −1362	−1395	0.44	
10	m-Acetaminophenyl	−1409	−1412	0.21	
11	m-Nitrophenyl	−1375	−1368	0.71	$E_{1/2}$ of NO$_2$ is −412 mV

trode at a potential of limiting diffuse current of wave i_{c2}. Isolated products were examined spectrophotometrically in both u.v. and i.r. regions. 3-Phenylrhodanine showed in the u.v. region two significant strongly intense absorption bands [18, 24—26]; the first of them at 258.5 nm was ascribed to the "N" conjugation, whereas the second one at 296.5 nm to the "S" conjugation. The product of reduction revealed only one prominent absorption maximum at 248.6 nm, as seen in Fig. 3. We assume that the C=S group is reduced during the electrode process and therefore neither "N" nor "S" conjugation could appear. The absorption band of the product of reduction could be asso-
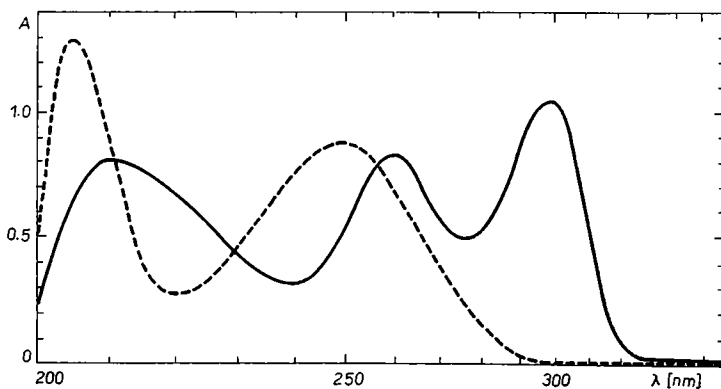

Fig. 3. Ultraviolet spectrum.

——— 5 × 10⁻⁵ M 3-phenylrhodanine in methanol; ········ product of reduction at a constant potential in methanol.

ciated with the amido grouping what means that reduction of the thione group took place during the electrode process.

Correctness of this presumption is evidenced also by i.r. spectra (Fig. 4): 3-Phenyl-rhodanine displayed notable vibration copulations at $\tilde{\nu}_1 = 1050$, $\tilde{\nu}_2 = 1385$, $\tilde{\nu}_3 = 1493$ cm^{-1} probably due to combination reactions of thioamide type derivatives, so-called "N=C=S" bands. The band of C=S stretching vibrations $\tilde{\nu}_4$ could be seen at 654 cm^{-1} and $\tilde{\nu}_5$ characteristic of a C=O group at 1730 cm^{-1}. The reduced product did not reveal any C=S stretching vibrations. Vibrations of the CH—SH grouping are very little pronounced in the i.r. spectrum, nonetheless their presence is evident. Of interest is the change in the wavenumber of the carbonyl group in the product of reduction in which the car-
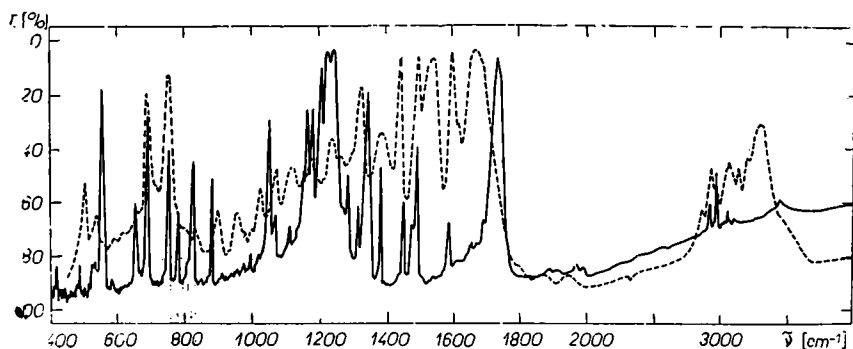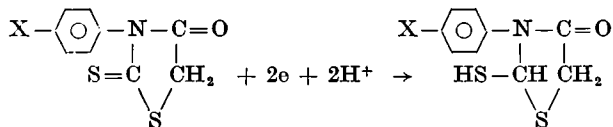

Fig. 4. Infrared spectrum.
———— 3-phenylrhodanine; · · · · · product of reduction.

bonyl band occurred at 1670 cm^{-1}. This shift could be caused either by intra- or inter-molecular hydrogen bonds between S and N, or the deformation vibration of the benzene ring became more pronounced.

Taking the above-mentioned observations into consideration, the mechanism of reduction of rhodanines on a mercury dropping electrode could be suggested:

$$X-\langle O \rangle-N-C=O \qquad\qquad X-\langle O \rangle-N-C=O$$
$$S=C \quad CH_2 \; + 2e + 2H^+ \;\rightarrow\; HS-CH \quad CH_2$$
$$\searrow\!\!\nearrow \qquad\qquad\qquad\qquad \searrow\!\!\nearrow$$
$$S \qquad\qquad\qquad\qquad\qquad S$$

This mechanism is in accordance with suggestions of *Dreux* and co-workers [13, 14].

The effect of substituents on the change of half-wave potential of 3-substituted derivatives of rhodanine was examined both in Britton—Robinson buffer solutions at pH 6.85 and in tetramethylammonium iodide as supporting electrolytes. The 0.05 M tetramethylammonium iodide solution in 50% methanol was adjusted to pH 6.8 with a 0.02 N-NaOH solution. Data thus obtained are listed in Table 3 and plotted in Fig. 5. The σ values were taken from [27]. Fig. 5 shows that $E_{1/2}$ values could well be correlated with σ values characterizing the substituent effect.

Fig. 5. Dependence of $E_{1/2}$ of 3-substituted derivatives of rhodanine on the σ value characterizing the substituent effect. $\circ$ $E_{1/2}$ values in Britton—Robinson buffer solution; $\square$ $E_{1/2}$ values in 0.05 M tetramethylammonium iodide.
Correlation coefficient $r = 0.96$ (the value of p-dimethylaminophenylrhodanine was not considered).
$\varrho = 0.071$ V.
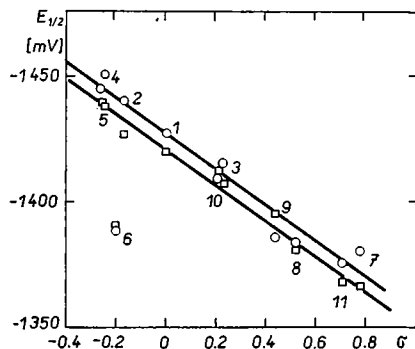
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