

Electrochemical study of the diethyldithiocarbamate anion and of its oxidation products

J. LABUDA, J. MOCÁK, and D. I. BUSTIN

Department of Analytical Chemistry, Slovak Technical University,
812 37 Bratislava

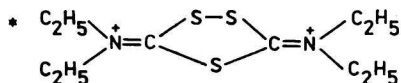
Received 27 November 1981

Study has been made of the voltammetric behaviour of the diethyldithiocarbamate anion, tetraethylthiuram disulfide, tetramethylthiuram monosulfide, sulfur, sodium sulfide, and of tetramethylthiourea on a platinum and mercury electrodes in acetonitrile and dimethylformamide. Findings have been supplemented by coulometric electrolysis results. A mechanism of processes of a deeper electrode oxidation of dithiocarbamates has been suggested and discussed.

Изучено вольтамперометрическое поведение диэтилдитиокарбаминатного аниона, тетраэтилтиурамдисульфида, тетраметилтиураммоносульфида, серы, сульфида натрия и тетраэтилтиомочевины на платиновом и ртутном электродах в ацетонитриле и диметилформамиде. Знания дополнены результатами кулонометрического электролиза. Предложен и обсужден механизм процессов более глубокого электроокисления дитиокарбаминатов.

It is widely known that unusual oxidation metal states can be stabilized by the dithiocarbamate ligand, which has proved to be of permanent interest. Thanks to the planary delocalized system this ligand, by its great donating ability, can raise electron density on a metal atom, in consequence of which there exist complexes of a formally high oxidation state of the central ion [1]. In some complexes, however, intramolecular redox processes occur, in which the central ion is reduced and the coordination sphere, formed by dithiocarbamate ligands, is oxidized.

It was in an attempt to explore the character of such processes that an examination of the electrochemical behaviour of the free diethyldithiocarbamate Et_2dtc^- ion on a platinum indicating electrode in acetonitrile was published [2]. The products obtained through successive oxidation of Et_2dtc^- (I): tetraethylthiuram disulfide – Et_4tds (II) and 3,5-bis(*N,N*-diethyliminum)trithiolane-1,2,4 dication – $\text{Et}_4\text{bitt}^{2+}$ (VI)*, are identical with species observed after the oxidation of



Zn, Cd, Hg [3—7], Ni [8—11], Fe, Co, Cu, Sb [7—12] dithiocarbamate complexes in their coordination sphere or in the decomposition products of this coordination sphere, as *e.g.* in the case of Co, Ru, Rh [13—16]. $\text{Et}_4\text{bit}^{2+}$ cation stability, however, is limited [2] and its reactivity has not been so far explored.

The present work aims at presenting fuller voltammetric characteristics of the Et_2dtc^- anion and of some products of its electrochemical oxidation, and, after the use of several kinds of indicating electrodes (Pt, DME, and hanging mercury-drop electrode — HMDE), two solvents with different solvation effect (acetonitrile, dimethylformamide) and electrolysis in the bulk phase of the solvent, at rating the resulting chemical reactions to which products of deeper Et_2dtc^- oxidation are liable.

Experimental

Voltammetric measurements were made with a three-electrode polarograph, Model OH-102 (Radelkis, Budapest). The working electrodes used were a platinum disc electrode (surface area 1.150 mm^2), sealed in soft glass, a hanging mercury-drop electrode of the Kemula E-69b type (Radiometer, Copenhagen) and, for polarographic measurements, a dropping mercury electrode (DME) with constants $t_1 = 4.8 \text{ s}$, $m = 1.4 \text{ mg s}^{-1}$. The reference electrode consisted of a calomel electrode in an aqueous LiCl solution of 4 mol dm^{-3} (4 MCE) with a 0.1 mol dm^{-3} salt bridge filled with tetrabutylamine tetrafluoroborate. The auxiliary electrode was a large surface platinum electrode. Unless otherwise stated in the text, the scan rate used in the stationary indicating electrode was $v = 0.1 \text{ V s}^{-1}$ and in polarography $v = 4.1 \times 10^{-3} \text{ V s}^{-1}$.

Coulometric measurements were made with a universal OH-404 coulometric analyzer (Radelkis, Budapest). The working electrode consisted of a double circular platinum gauze, placed parallel to a frit separating the anodic from the cathode compartment in the electrolytic cell. The auxiliary electrode was a platinum coil. The reference electrode was constituted as for voltammetric measurements.

Inert gas, employed in voltammetric and coulometric measurements, was incandescent lamp nitrogen dehydrated in anhydrous CaCl_2 and saturated with the vapours of the used solvent.

Acetonitrile (Avondale Laboratories, England) and dimethylformamide (Reachim, the USSR) were purified as described in [17] or [18].

Tetrabutylamine tetrafluoroborate (Southwestern Analytical Chemicals, Austin, Texas) in 0.1 mol dm^{-3} concentration was used as base electrolyte.

Sodium diethyldithiocarbamate (Lachema, Brno) was recrystallized twice from ethanol, as was the tetraethylthiuram disulfide (*II*) (Robac, Robinson Brothers, England). As tetraethylthiuram monosulfide is not being commercially produced, use was made of tetramethylthiuram monosulfide (*III*) (Robinson Brothers, England) after being twice recrystallized from ethanol. Tetramethylthiourea was prepared on site by the pyrolysis of tetramethylthiuram disulfide and purified by being recrystallized from chloroform solution

in the presence of activated carbon. Sulfur and sodium sulfide were of reagent grade (Lachema, Brno).

Results and discussion

Sodium diethyldithiocarbamate — NaEt_2dtc

Primary redox processes (Table 1) are connected with Na^+ reduction on the Pt or Hg electrode (Peak H, Fig. 1) and with the Et_2dtc^- anion (I) oxidation on Pt (Peak A, Fig. 1). The oxidation process was the next to be examined. Coulometric electrolysis carried out at a potential of +0.4 V confirmed that the number of

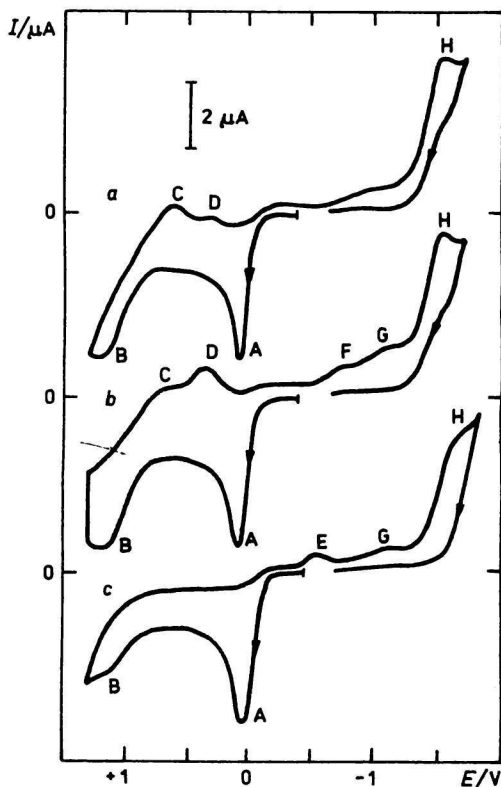


Fig. 1. Cyclic voltammograms of $1 \times 10^{-3} \text{ mol dm}^{-3} \text{ Et}_2\text{dtc}^-$.

a) In acetonitrile; b) as a) with the stop of sweep at +1.3 V vs. 4 MCE for 10 s; c) in dimethylformamide.

Pt electrode, scan rate 0.1 V s^{-1} , $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NBF}_4$.

Table 1

Voltammetric characteristics of the studied species (V vs. 4 MCE)

Substance	Reduction						Oxidation			
	Pt		HMDE		DME		Pt	HMDE	DME	
	$E_{p,1}$	$E_{p,2}$	$E_{p,1}$	$E_{p,2}$	$E_{1/2,1}$	$E_{1/2,2}$	$E_{p,1}$	$E_{p,2}$	E_p	$E_{1/2}$
Acetonitrile										
Et ₂ dte ⁻ (Na ⁺)	-1.65		-1.90		-1.85		+0.10	+1.10	-0.50	-0.55
Et ₄ tds	-1.80		-0.70		-0.65		+0.85			
Me ₄ tms	-2.10		-1.85		-1.75		+0.85			
S	-0.80	-1.50	-0.90	-1.30	-0.80	-1.25	+1.70			
Na ₂ S	-1.60		-1.85		-1.80		+0.20		+0.05	-0.05
Me ₄ tu							+0.60			
H ⁺ (HClO ₄)	-0.50		-1.20		-1.10					
Dimethylformamide										
Et ₂ dte ⁻ (Na ⁺)	-1.75		-1.95		-1.90		+0.10	+1.20	-0.50	-0.55
Et ₄ tds	-1.80		-0.70		-0.65		+1.10			
Me ₄ tms	-1.90		-1.80		-1.70		+0.95			
S	-0.80	-1.45	-0.95	-1.35	-0.90	-1.30	+1.30			
Na ₂ S	-1.70		-1.95		-1.90		+0.20			
Me ₄ tu							+0.60			
H ⁺ (HClO ₄)	-0.60	-1.05	-1.40		-1.30					

exchanged electrons of electrochemical oxidation of *I* equals 1. Voltammetric analysis of the electrolyzed product (see below) revealed the presence of Et₄tds (*II*), resulting, according to [19, 20] from the dimerization of the oxidation primary product.

On the DME, *I* is characterized by an anodic wave ($E_{1/2} = -0.55$ V) due to the electrode material oxidation in the presence of *I* [21, 22].

A further degree of voltammetric *I* oxidation on Pt in acetonitrile has been revealed by a broad peak B in the range of +1.1 to +1.3 V (Fig. 1a). The cathodic part of the cyclic voltammogram is dependent on the time of electrode polarization (Fig. 1b). Cathodic peaks of small size, which vary with time, indicate that a deeper oxidation of the *I* anion gets complicated by slow chemical reaction producing several electroactive species. These processes may be accounted for, with regard to the later mentioned study and in keeping with [2], as follows: It is a chemical reaction inserted between two electrochemical processes (ECE mechanism). In step 1 oxidation of the species *II* occurs with one electron exchange during the formation of 3,6-bis(*N,N*-diethyliminium)tetrathiolane-1,2,4,5 monocation (*IV*) yielding a cathodic peak at +0.60 V (which corresponds to Peak C in Fig. 1 we have observed). In the second chemical step, according to [2], sulfur, characterized by a cathodic peak at -0.8 V (Peak F), splits off giving rise to 3,5-bis(*N,N*-diethyliminium)trithiolane-1,2,4 monocation (*V*). In step 3, in losing one electron, *V* passes on to Et₄bitt²⁺ (*VI*) yielding a cathodic peak at +0.25 V (Peak D).

The recorded process of deeper *I* oxidation in dimethylformamide is different (Fig. 1c). The character of these modifications was further verified by the study of Et₄tds.

Tetraethylthiuram disulfide — Et₄tds (II)

Voltammetric characteristics are again given in Table 1. Species *I* results from the reduction of *II* at $E_p = -1.8$ V.

The oxidation of *II* has its peak at $E_p = +0.85$ V, splitting in some experiments into two parts, the second extending as far as to +1.1 V.

The cathodic portions of cyclic voltammograms, observed both in acetonitrile and dimethylformamide after the oxidation of *II* and the scan reversal, coincide with the record obtained after a deeper oxidation of *I* sodium salt (Fig. 1a—c), and in addition contain only the disulfide bond reduction peak (on Pt at -1.8 V) evidently in the absence of the Na⁺ reduction peak (Peak H). The mechanism of electrochemical *II* oxidation in dimethylformamide was verified by examining the dependence of the I_p peak current of anodic peak B (at +1.2 V) on scan rate v . With the decrease in the scan rate within the range of $1.0 \times 10^{-1} - 1.25 \times 10^{-2}$ V s⁻¹, the value of the $I_p/v^{1/2}$ ratio increases resulting in the rise of the

observed number of exchanged electrons. The electrode oxidation of *II* in dimethylformamide is, therefore, complicated by the inserted chemical reaction just as it was in acetonitrile. The difference in voltammetric records when using the mentioned solvents is evidently due to the increased rate in the ECE mechanism chemical step and to a lower $\text{Et}_4\text{bitt}^{2+}$ (*VI*) stability. Reduced *VI* stability in dimethylformamide may have some connection with electron-donating properties of the solvent or even with the content of reduction impurities.

Coulometric oxidation of *II*, in either solvent at a constant potential of +1.15 V carried out until steady state background current was achieved yielded the value of the number of exchanged electrons slightly exceeding 2. However, it was not a quantitative oxidation, a slightly anodic peak tenaciously persisting on the voltammogram. A recording made after electrolysis together with its time change is shown in Fig. 2. Conclusions derived from voltammetric study of the decomposition rate of *VI* were confirmed by the coulometric *II* oxidation carried out in dimethylformamide (Fig. 2c).

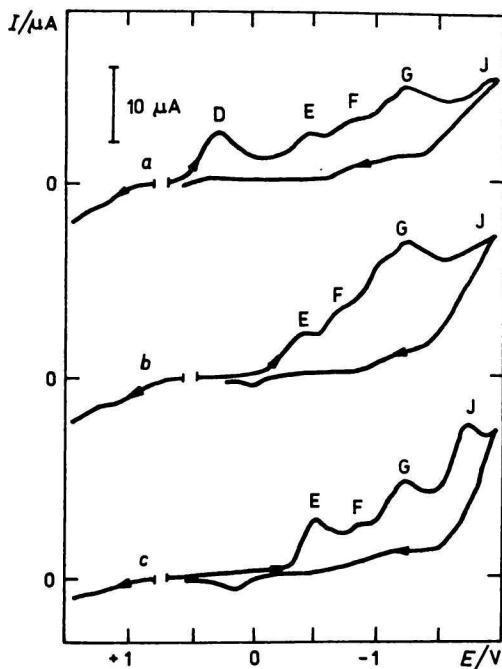


Fig. 2. Bulk-phase electrooxidation products of $2 \times 10^{-3} \text{ mol dm}^{-3} \text{ Et}_4\text{tds}$. Electrolysis at +1.15 V vs. 4 MCE finished after the charge corresponding to two-electron oxidation was supplied by potentiostat. Voltammograms a) acetonitrile solution, 3 min after electrolysis; voltammograms b) acetonitrile solution, 180 min after electrolysis; voltammograms c) dimethylformamide solution, 3 min after electrolysis. Pt electrode, scan rate 0.1 V s^{-1} , $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NBF}_4$.

The electrochemical behaviour of *II*, prepared *in situ* by the electrolytic *I* oxidation was the same as that in the above-mentioned study of the synthetically prepared *II*.

Tetramethylthiuram monosulfide — Me₄tms (*III*)

The characteristic data are given in Table 1. One of its reduction products at $E_p = -2.1$ V is the Me₂dtc⁻ free ion. The cathodic counterpeak at +0.30—+0.25 V (in dimethylformamide observable only at higher scan rates) belongs to voltammetric oxidation product ($E_p = +0.85$ V). The anodic peak current of *III* varies linearly with the square root of the scan rate and this dependence runs through the origin of the system of coordinates. The oxidation process is, therefore, diffusion-controlled.

By coulometric electrolysis, carried out at a constant potential of +1.0 V, two-electron oxidation of *III* has in principle been confirmed. The primary product of the oxidation is, therefore, a particle having a total charge of 2+, evidently Me₄bitt²⁺. The reduction part of voltammogram of electrolyzed solution was identical with the general picture after the oxidation of *II*, with the exception of the absence of free sulfur peak at -0.8 V (see below). It also showed similar time changes. Fig. 3a demonstrates such a voltammogram in dimethylformamide. The

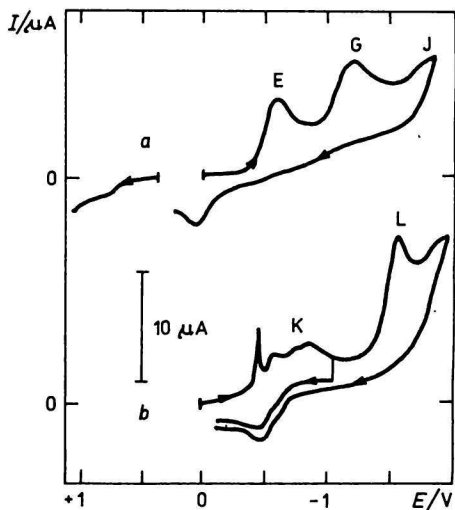


Fig. 3. Cyclic voltammograms of bulk-phase electrooxidation products of 2×10^{-3} mol dm⁻³ Me₄tms. Electrolysis at +1.1 V vs. 4 MCE finished after the charge corresponding to two-electron oxidation was supplied by potentiostat.

a) Pt electrode; b) HMDE. Scan rate 0.1 V s⁻¹, 0.1 mol dm⁻³ Bu₄NBF₄ in dimethylformamide.

rate constant of $\text{Me}_4\text{bitt}^{2+}$ decomposition was determined in acetonitrile (note peak D current decrease at +0.25 V) to be: $d \ln I_p/dt = 1.0 \times 10^{-3} \text{ s}^{-1}$, a comparable rate constant also characterizing the simultaneous cathodic peak G current rise (at -1.2 V).

After a subsequent electrolytic reduction of the bulk solvent phase with a Pt electrode at a constant potential of -0.8 V there was no Peak E (-0.55 V) on the voltammogram obtained with a Pt indicating electrode, and on the recording done with a HMDE the height of Peak L (at -1.6 V) considerably decreased. Both cathodic peaks (E and L) may belong to the electrochemical change of the same species, which will be discussed later. After further electrolytic reduction on a Pt electrode at a constant potential of -1.4 V reducing the substance characterized by voltammetric peak G at -1.2 V (Fig. 3a) there was present in the solvent a free ion of Me_2dtc^- identified by an anodic peak both on the Pt (+0.1 V) and the HMDE (-0.55 V).

Sulfur

The first reduction step (Table 1) on a Pt electrode ($E_p = -0.8 \text{ V}$) in acetonitrile is characterized by an anodic counterpeak of a larger potential range at -0.2 V, the second cathodic peak at $E_p = -1.5 \text{ V}$ having an anodic counterpeak at -1.1 V. In dimethylformamide anodic counterpeaks are by about 0.1 V more positive than the corresponding peaks in acetonitrile. The shape of either cathodic peak as well as the potential position and currents of their anodic counterpeaks are all evidence of perceptible irreversibility (contrary to what has been asserted in paper [2]). In between the two mentioned cathodic peaks there was a changeable but ever a small peak at -1.05 V. Sulfur oxidation (Table 1) is also irreversible.

An electrolytic reduction was carried out in the bulk solvent phase at a constant potential of -1 V. The expected sulfide anions have yielded an anodic peak at 0 V in acetonitrile and at +0.05 V in dimethylformamide.

Tetramethylthiourea — Me_4tu

While tetramethylthiourea itself is a nonreducing species, after its voltammetric oxidation at +0.6 V, however, a cathodic counterpeak at +0.1 V was registered, the maximum currents ratio of anodic to cathodic peaks being close to 1. The number of exchanged electrons of its electrochemical oxidation, $n = 1$, was determined through coulometric electrolysis carried out at constant potential +0.8 V.

*Mechanism proposed for electrochemical processes observed
in cyclic voltammetry*

Oxidation of both *II* and *III* leads to the formation of derivatives of the trithiolane dication (*VI*), characterized by cathodic peak D. The said reduction (Peak D) gives rise to tetraalkylthiuram monosulfide (*III*).

The cathodic peak E at -0.55 V, which was found on all the voltammograms recorded by the Pt electrode after preceding oxidation in the region of over $+1$ V, is ascribed to H^+ reduction which is the solvent oxidation product [24].

On a mercury electrode (Peak L) a reduction of H^+ takes place in consequence of H^+ over-voltage at a more negative potential of about 1 V (Table 1). Relatively large current of Peak E, in view of the charge used up in electrolysis, indicates that the proton has originated not only electrochemically but also through the chemical reaction of species *IV*, *V*, *VI* (i.e. of cationic products of the oxidation of *II* and *III*) with the solvent and the residual water contained in it.

Peak F ($E_p = -0.8$ V) belongs to the reduction of sulfur released during the conversion of *IV* into *V* as described above. During the decomposition process of Et_4bitt^{2+} (*VI*), however, and contrary to the assertion in [2] we failed to register any conspicuous increase in this peak. Our observations have also disproved the view expressed in [25] that sulfur is not released in deep oxidation of *I*.

Peak G, registered by a Pt electrode in the region of -1.2 V represents the reduction of the product resulting from the chemical reaction of the Et_4bitt^{2+} cation (*VI*). This product is stable in both the solvents employed and, as was proved by voltammetry on Pt and Hg electrodes, contains the evidently preserved structural Et_2dtc unit. The assumption in paper [2] has not been confirmed, viz. that Peak G belongs only to the reduction of the sulfur anion. Sulfur, however, may, by its reduction observed at -1.05 V, have contributed to the cathodic current in the potential region under study.

When the HMDE was used, Peak G was missing on voltammograms. A smaller cathodic peak K, however, was recorded in the region of -0.7 V, connected with the formation of a free dithiocarbamate anion. This peak as well as Peak J is a proof that the disulfide bond is preserved at least in parts of the reaction products of *VI*.

None of the observed peaks can be attributed to tetraethylthiourea (nor to its oxidized form) [23].

The oxidation of reaction products combined with the partial oxidation of the solvent, increases the charge needed in coulometric experiments, being the cause of the persistence of a certain anodic current in the region of $+1$ V during the electrolytic oxidation process of *II* and *III* or of its increase after the termination of electrolysis, although such an increase was observed to a much lesser degree than is claimed in [2].

References

1. Willemse, J., Cras, J. A., Steggerda, J. J., and Keijzers, C. P., *Structure and Bonding* 28, 84 (1976).
2. Scrimager, C. and De Hayes, L. Y., *Inorg. Nucl. Chem. Lett.* 14, 125 (1978).
3. Brinkhoff, H. C., *Thesis*. Nijmegen, 1970.
4. Brinkhoff, H. C., Cras, J. A., Steggerda, J. J., and Willemse, J., *Rec. Trav. Chim Pays-Bas* 88, 633 (1969).
5. Brinkhoff, H. C., Grotens, A. M., and Steggerda, J. J., *Rec. Trav. Chim. Pays-Bas* 89, 11 (1970).
6. Beurskens, P. T., Bosman, W. P. J. H., and Cras, J. A., *J. Cryst. Mol. Struct.* 2, 183 (1972).
7. Willemse, J., *Thesis*. Nijmegen, 1974.
8. Avdeef, A., Fackler, J. P., and Fisher, R. G., *J. Amer. Chem. Soc.* 92, 6972 (1970).
9. Hendrickson, A. R., Martin, R. L., and Rohde, N. M., *Inorg. Chem.* 14, 2980 (1975).
10. Budnikov, G., Ulakhovich, N. A., and Koshurnikova, I. V., *Zh. Obshch. Khim.* 46, 1420 (1976).
11. Budnikov, G., Ulakhovich, N. A., Kargina, O. Yu., and Fomina, L. G., *Zh. Obshch. Khim.* 48, 1667 (1978).
12. Willemse, J. and Steggerda, J. J., *Chem. Commun.* 1969, 1123.
13. Gahan, L. R. and O'Connor, M. S., *Chem. Commun.* 1974, 68.
14. Hendrickson, A. R., Martin, R. L., and Taylor, D., *Aust. J. Chem.* 29, 269 (1976).
15. Mattson, B. M., Heiman, J. R., and Pignolet, L. H., *Inorg. Chem.* 15, 564 (1976).
16. Wheeler, S. H., Mattson, B. M., Miessler, G. L., and Pignolet, L. H., *Inorg. Chem.* 17, 340 (1978).
17. Coetzee, J. F., Cunningham, G. P., McGuire, D. K., and Padmanabhan, G. R., *Anal. Chem.* 34, 1139 (1962).
18. Thomas, A. B. and Rochow, E. G., *J. Amer. Chem. Soc.* 79, 1843 (1957).
19. Cauquis, G. and Lachenal, D., *J. Electroanal. Chem.* 43, 205 (1973).
20. Cauquis, G. and Lachenal, D., *J. Electroanal. Chem.* 57, 141 (1974).
21. Halls, D., Townshend, A., and Zuman, P., *Anal. Chim. Acta* 41, 51 (1968).
22. Bond, A. M., Casey, A. T., and Thac Keray, J. R., *Inorg. Chem.* 12, 887 (1973).
23. Thorn, G. D. and Ludwig, M. A., *The Dithiocarbamates and Related Compounds*. Elsevier, Amsterdam, 1962.
24. Mann, Ch., *Electroanal. Chem.* 3, 57 (1969).
25. Usatenko, Yu. I. and Galushko, S. V., *Elektrokhimiya* 12, 84 (1976).

Translated by J. Dravecký