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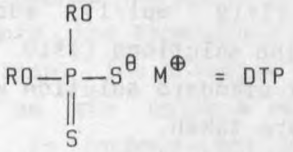
COULOMETRIC DETERMINATION OF DITHIOPHOSPHATES WITH THE USE OF THE INDUCED IODINE-AZIDE REACTION

The characteristics of potassium diethyl- and dibuthyl-dithiophosphates as the inductors of iodine-azide reaction carried out electrolytically have been presented. The influence of the pH and concentrations of azide and iodide ions on the course of reaction was examined. The determinations have been carried out in the range of 1-20 nmol.

Dithiophosphates (DTP) are used as pesticides [1], additives to lubricants and anticorrosion agents [2] and also as flotation collectors for sulfide minerals [3].



$$RO-\overset{RO}{\underset{\overset{\|}{S}}{P}}-S^{\ominus}\ M^{\oplus} = DTP$$

Due to such a broad range of application of dithiophosphates this group has become an important object of analytical research. Dithiophosphates can be determined using titration methods (iodometric [4] and argentometric [5]) as well as spectrophotometric [,1, 3, 4] and polarographic methods [6]. A coulometric method of the determination of dithiophosphates based on the measurement of the electric charge necessary for

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the generation of the iodine taking part in the induced reaction as been presented. The technique of coulometric titration had previously been used for the determination of a number of sulphur compounds inducing the iodine-azide reaction [7-9].

EXPERIMENTAL

REAGENTS, SOLUTIONS AND APPARATUS

Twice distilled water in glass apparatus.

Sodium azide, pure; solution containing 200 g NaN_3 per litre.

Potassium iodide, analytical-reagent grade, 0.1 mol/l.

Hydrochloric acid, analytical-reagent grade, 1 mol/l.

Potassium diethyldithiophosphate (DEDTP, $R = C_2H_5$) and potassium dibuthyldithiophosphate (DBDTP, $R = nC_4H_9$), synthesized in the Department of Instrumental Analysis Institute of Chemistry, Adam Mickiewicz University, Poznań, Poland; the exact content of dithiophosphates in the reagents was determined by potentiometric titration with standard silver nitrate solution [5].

Standard solutions ($1*10^{-3}$ mol/l) of DEDTP and DBDTP, containing natrium hydroxide ($1*10^{-3}$ mol/l), added in order to eliminate hydrolysis; working solutions ($1*10^{-4}$ or $5*10^{-5}$ mol/l), prepared by diluting the standard solution with water directly before the measurements were taken.

Reaction solution I containing sodium azide (20 g per litre), potassium iodide ($3*10^{-3}$ mol/l), and the amount of hydrochloric acid to reach pH = 6.0.

Reaction solution II containing sodium azide (50 g per litre), potassium iodide ($3*10^{-3}$ mol/l), and the amount of hydrochloric acid to reach pH = 6.0.

Universal coulometric analyser Radelkis, type OH-404.

Electrolysis cell with two platinum electrodes of the area 5 cm^2 each, working in generating circuit and with a double electrode type OH-9381 in an amperometric indicator-circuit with two polarized electrodes (mechanical stirrer; automatic pipettes with capacities of 10, 20, 50 and 100μl).

THE CHARACTERISTICS OF THE IODINE-AZIDE REACTION INDUCED BY DEDTP AND DBDTP

In order to choose the optimum conditions of inducing of the iodine-azide reaction with dithiophosphates, the influence of the pH of the solution, of the concentration of potassium iodide, of the concentration of sodium azide, and of the current on the course of coulometric titration was investigated. Since the rate of the iodine-azide reaction induced by dithiophosphates is relatively low, in order to titrate the entire amount of the inductor the delay time of the analyser was set at 30 s. That made it possible to switch on the current in the generating circuit again, when in 30 s as a result of the reaction the indicator-current decreased below the assumed value of 2 μA, at which the current in the generating circuit was stopped automatically.

The dependence of the electric charge needed to generate the amount of iodine necessary for the titration on the conditions in which the experiment was conducted is presented on three consecutive diagrams. The value ΔQ on the Y-axis is the difference between the electric charges used in the presence and in the absence of the inductor until the indicator-current reaches the value of 2 μA, at delay time 30 s.

Figure 1 presents the dependence of the electric charge on the pH of the solution. The pH-value 6.0 at which ΔQ is high has been chosen as the optimum value. The use of solutions whose pH is lower is inconvenient because of the emission of the poisonous, volatile hydrazoic acid.

Figure 2 presents the influence of the concentration of sodium azide on the electric change in the reaction induced by DEDTP. For this compound, changes of the generating current between 0.5 and 5 mA do not affect the electric change, which is proportional to the amount of the inductor within the range of 1-20 nmol in the sample.

Figure 3 presents the influence of the concentration of azide and of the current on the electric change (ΔQ) in the reaction induced by DBDTP. In the solution containing NaN_3 at the concentration of 20 g per litre rectilinear dependence of the electric charge on the amount of the inductor is observed

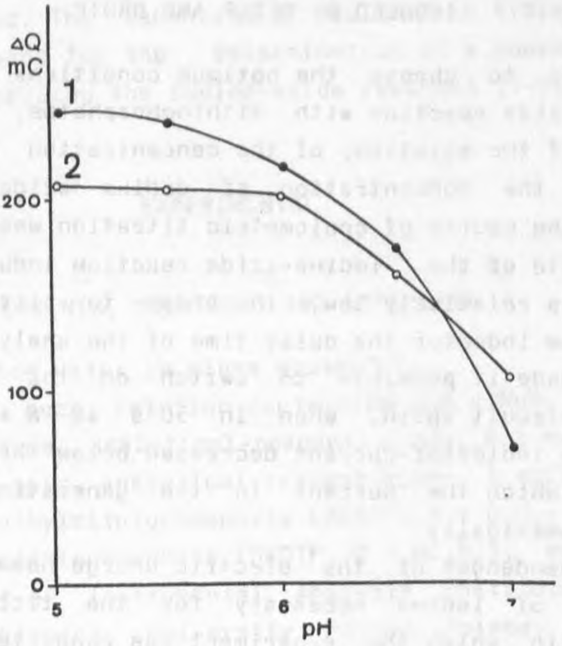


Fig 1. Relation between the electric charge and the pH of solution (20 g NaN_3 per litre, $3*10^{-3}$ mol/l KI)

1 - 10 nmol $(C_2H_5O)_2PSSK$, I = 1 mA; 2 - 10 nmol $(C_4H_9O)_2PSSK$, I = 5 mA

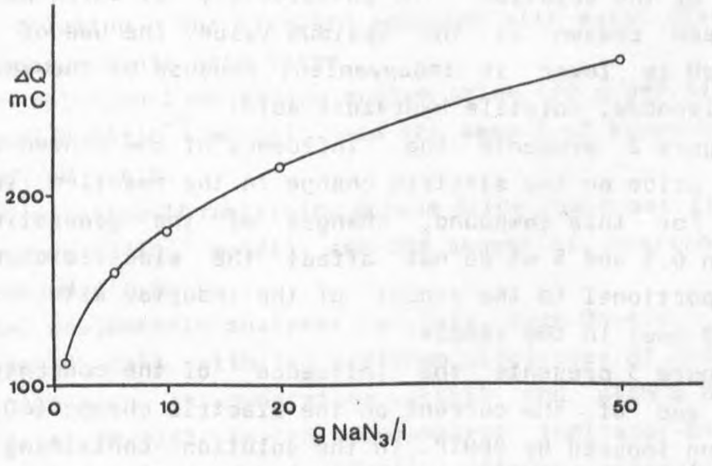


Fig. 2. Relation between the electric charge and the concentration of NaN_3(10 nmol $(C_2H_5O)_2PSSK$, pH = 6.0, $3*10^{-3}$ mol/l KI)

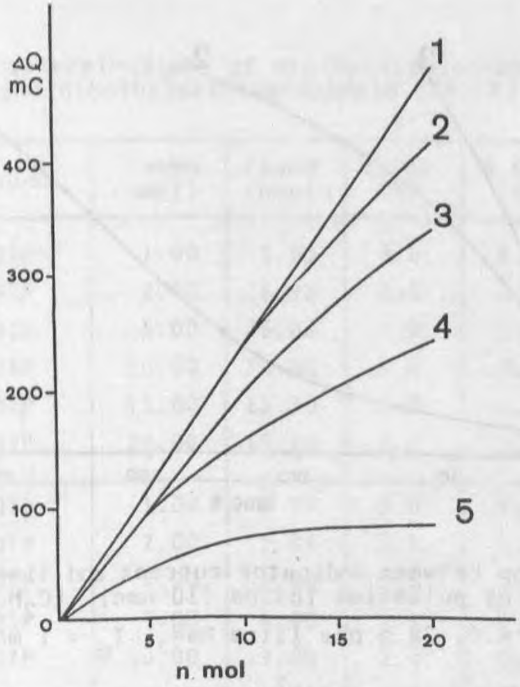


Fig. 3 Relation between the electric charge and the amount of $(C_4H_9O)_2PSSK$ (pH = 6.0, $3*10^{-3}$ mol/l KI)

1 - $\varrho(NaN_3)$ = 50 g/l, I_{gen} = 5 mA; 2 - $\varrho(NaN_3)$ = 50 g/l, I_{gen} = = 1 mA; 3 - $\varrho(NaN_3)$ = 20 g/l, I_{gen} = 5 mA; 4 - $\varrho(NaN_3)$ = 20 g/l, I_{gen} = 1 mA; 5 - $\varrho(NaN_3)$ = 5 g/l, I_{gen} = 1 mA

only till the amount of 10 nmol in the sample (for I = 5 mA) is reached; this line may serve as the calibration line in the determination of dibuthyldithiophosphate in the range of 1-10 nmol. The determination of DBDTP in the range of 1-20 nmol should be conduced in a solution containing sodium azide at the concentration of 50 g per litre, at I = 5 mA.

The dependence of the indicator-current on time for different concentrations of iodide in the titration of DEDTP (Fig. 4) shows that the rate of the induced reaction decreases with increasing concentration of iodide ions. At the same time, the growth of the concentration of KI causes the decrease of the

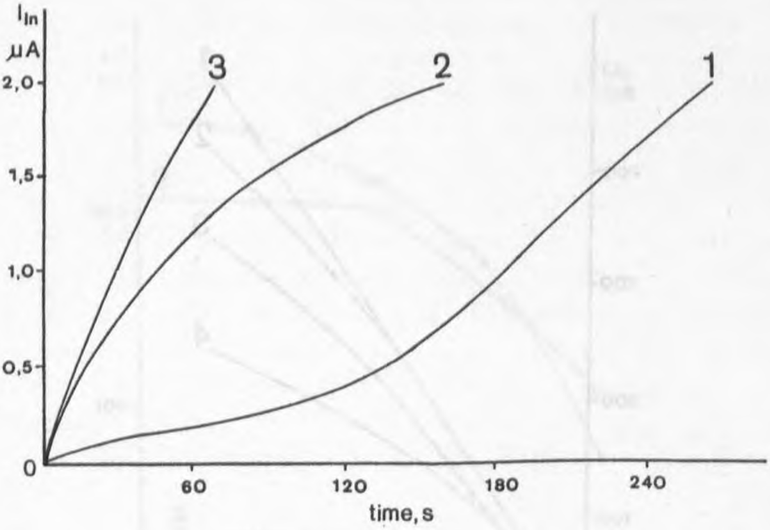


Fig. 4. Relation between indicator current and time for different concentrations of potassium iodide (10 nmol $(C_2H_5O)_2PSSK$, pH = = 6.0, 20 g per litre NaN_3, I_g = 1 mA)

1 - $3*10^{-3}$ mol/l KI; 2 - $1*10^{-2}$ mol/l KI; 3 - $3*10^{-2}$ mol/l KI

use of iodine. Similar relationships were obtained for DBDTP. No measurements were taken in solutions containing iodide at concentrations below $3*10^{-3}$ mol/l, because the non-induced iodine-azide reaction takes place.

MEASUREMENTS

The determination of diethyldithiophosphate was conducted in reaction solution I at the generating current of 1 mA, and the determinations of dibuthyldithiophosphate in reaction solutions I and II at the current of 5 mA. In the case of the titration with the current of 5 mA, in order to determine the end point more precisely, the apparatus was programmed to automatically lower the current in the generating circuit ten times at the moment when the indicator-current reached the value of 1.8 μA.

Table 1

Results of the determination of diethyldithiophosphate (DEDTP) and dibuthyldithiophosphate (DBDTP)

Nr	Compound	Taken (nmol)	Found (nmol)	Error (%)	R.S.D. (%)	Reaction solution
1	DEDTP	1.00	1.03	3.0	8.5	I
2	DEDTP	2.00	1.96	2.0	4.8	I
3	DEDTP	5.00	5.06	1.2	2.7	I
4	DEDTP	10.00	10.00	0.0	2.4	I
5	DEDTP	15.00	15.30	2.0	1.6	I
6	DEDTP	20.00	19.70	1.5	2.0	I
7	DBDTP	1.00	0.97	3.0	9.2	I
8	DBDTP	2.00	2.04	2.0	5.5	I
9	DBDTP	4.00	4.06	1.5	3.7	I
10	DBDTP	7.00	6.90	1.4	2.2	I
11	DBDTP	10.00	9.80	2.0	2.4	I
12	DBDTP	1.00	1.01	1.0	7.7	II
13	DBDTP	2.00	2.01	0.5	4.9	II
14	DBDTP	5.00	4.92	1.6	3.8	II
15	DBDTP	10.00	10.10	1.0	4.0	II
16	DBDTP	15.00	15.00	0.0	2.3	II
17	DBDTP	20.00	19.60	2.0	2.1	II

n = 6.
R.S.D. - relative standard deviation.

A sample of the inductor was introduced into 20 ml of the reaction solution, placed in the anode part of the electrolysis cell; after starting the mechanical stirrer the direct current of 1 or 5 mA was being passed through the solution. The electric charge (Q) was noted after the entire amount of the inductor had been titrated and the apparatus had been switched off automatically, which happened after the current in the indicator circuit had reached the value of 2 μA at the delay time of 30 s. Then the charge Q_o was noted in a solution containing no inductor. The dependence of $\Delta Q = Q - Q_o$ on the amount of the inductors serves as calibration lines.

The results of the determinations have been presented in Tab. 1.

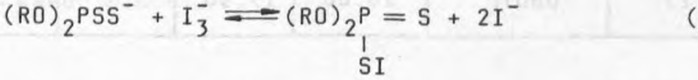
RESULTS AND CONCLUSIONS

The presented coulometric method permits the determination of 1-20 nmols of diethyl- and dibuthyldithiophosphate as inductors of the iodine-azide reaction.

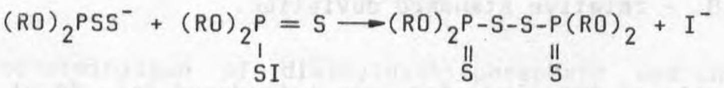
The induction coefficient, indicating how many times the amount of iodine used in the induced reaction is greater than in the ordinary iodometric reaction, in the conditions used (pH = 6.0, $3*10^{-3}$ mol/l KI) depens on the concentration of sodium azide and reaches for DEDTP and DBDTP the values 220 and 210 (20 g NaN_3 per litre) and 275 and 255 (50 g NaN_3 per litre), respectively.

The shape of the curves representing the electric charge as a function of the amount of dibuthyldithiophosphate (Fig. 3) can be explained on the basis of the assumed mechanism of the reaction:

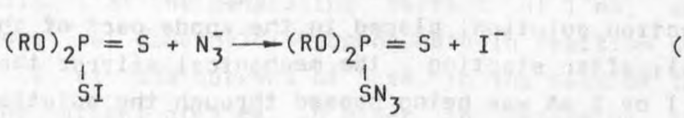
$$I_3^- + N_3^- \rightleftharpoons I_2N_3^- + I^- \quad (1)$$



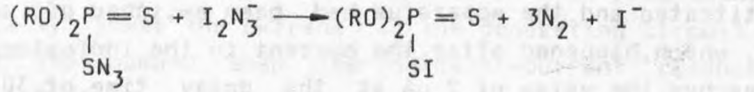
$$(RO)_2PSS^- + I_3^- \rightleftharpoons (RO)_2\underset{\substack{|\\ SI}}{P} = S + 2I^- \quad (2)$$



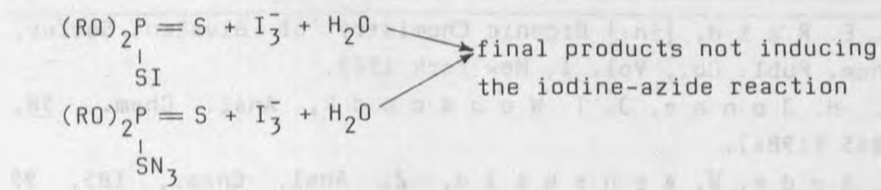
$$(RO)_2PSS^- + (RO)_2\underset{\substack{|\\ SI}}{P} = S \longrightarrow (RO)_2P\text{-}S\text{-}S\text{-}\underset{\substack{\|\\ S}}{P}(RO)_2 + I^- \quad (3)$$



$$(RO)_2\underset{\substack{|\\ SI}}{P} = S + N_3^- \longrightarrow (RO)_2\underset{\substack{|\\ SN_3}}{P} = S + I^- \quad (4)$$



$$(RO)_2\underset{\substack{|\\ SN_3}}{P} = S + I_2N_3^- \longrightarrow (RO)_2\underset{\substack{|\\ SI}}{P} = S + 3N_2 + I^- \quad (5)$$



$$\left.\begin{array}{l}(RO)_2\underset{SI}{\underset{|}{P}}=S + I_3^- + H_2O\\ (RO)_2\underset{SN_3}{\underset{|}{P}}=S + I_3^- + H_2O\end{array}\right\} \rightarrow \text{final products not inducing the iodine-azide reaction}$$

The deviation from the rectilinear dependence of the charge as a function of the concentration of $(C_4H_9O)_2PSSK$ can be explained by the occurrence of reaction 3; the higher the initial concentration of the inductor, the greater part of it is transformed into the non-active disulphide and in this way a certain amount of DBDTP does not take part in further steps of the induced reaction. The increase of the concentration of azide causes the increase of the rate of reaction 4 and, consequently, the elimination of reaction 3. The increase of the generating current causes a quicker formation of iodine and, in consequence, a quick transformation of the entire amount of DBDTP into a compound with iodine (reaction 2). The absence of dithiophosphate renders reaction 3 impossible. A similar phenomenon was observed in the coulometric determination of cysteine [8].

In the case of DEDTP no deviation from the rectilinear character of the dependence of the electric charge on the amount of the inductor is observed, which may be connected with the relative small role of reaction 3 in the mechanism presented above.

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KULOMETRYCZNE OZNACZANIE DITIOFOSFORANÓW Z WYKORZYSTANIEM INDUKOWANEJ REAKCJI JODO-AZYDKOWEJ

Przedstawiono charakterystykę dietylo- i dibutyloditiofosforanów jako induktorów reakcji jodo-azydkowej. Zbadano wpływ pH oraz stężeń azydku i jodku na przebieg reakcji. Oznaczenia kulometryczne przeprowadzono w zakresie 1-20 nmoli w próbce.