POLAROGRAPHIC DETERMINATION OF SOME NITRO GROUP-CONTAINING PESTICIDES

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Dedicated to Academician J. Mostecký on the occasion of his 60th birthday.

The differential pulse polarography technique was applied to the determination of some pesticides containing nitro groups in their molecules. The nitro groups were found to be reduced to hydroxylamines or to the corresponding amines. The effect of medium, particularly of pH of the supporting electrolyte, was examined. The pesticides were determined in concentrations less than 10 $\mu g\, l^{-1}$, which shows primose for the application of the technique to environmental water purity monitoring.

Polarographic methods can be used to advantage for the determination of agrochemicals in food, fodder, waters, body fluids, *etc.*, particularly if the pollutants contain nitro groups in their molecules. The nitro group are reduced with the participation of four electrons to the corresponding hydroxylamines, or with the participation of six electrons as far as the amines. At pH 6·09, 2-nitrophenol and 4-nitrophenol were observed to be reduced to the amines, 3-nitrophenol, only to hydroxylamine[1,2].

Many pesticides containing a nitro group, *e.g.* parathione and methylparathione[3,4], phenitrothione[5,6], or some dinitro pesticides[7–9] have been subject to polarographic study. The small differences in the peak potentials do not enable the nitro pesticides to be determined polarographically in mixtures; this difficulty has been circumvented by employing the polarographic technique only after a liquid chromatographic[10,11] or thin layer chromatographic[12] separation of the components.

An important work is that of Smyth and Osteryoung[3], who studied in detail the behaviour of parathione, methyl parathione, paraoxone, 4-nitrophenol, and pentachloronitrobenzene by pulse polarography in Britton–Robinson buffers of different pH as the supporting electrolyte. The polarographic behaviour of sulphur-containing pesticides differed markedly from that of the remaining substances due to their strong adsorption properties. The limit of determination attained was $1 \cdot 10^{-8}$ mol l^{-1}.

In the present work, four pesticides containing nitro groups in their molecules were studied with the aim to establish the character of their polarographic behaviour, to examine the possibility of determination of the individual substances in a mixture, and to attain a low limit of their determination.

EXPERIMENTAL

Chemicals and Solutions

Chemicals of reagent grade purity were used for the preparation of the supporting electrolytes, dissolution of samples, and chromatographic separation. The aqueous solutions were made up from isothermally redistilled water. 0·05M-H_2SO_4 solution (pH 1·15) and Britton–Robinson buffers served as the supporting electrolytes. The buffer selected as the most suitable (pH 6·1) was purified by electrolysis at a constant potential on a mercury pool electrode.

The following pesticides were studied: DNOK (2-methyl-4,6-dinitrophenol), Dinobutone (2-(1-methylpropyl)4,6-dinitrophenylcarbonate), CDT (4-chloro-3,5-dinitrotrifluorotoluene), and Metatione E50 (containing 50% phenitrothione) (O,O-dimethyl-O-(3-methyl-4-nitrophenyl) thiophosphate). The stock solutions of CDT and Dinobutone contained 500 mg of substance in a litre of methanol, the stock solution of DNOK was obtained by dissolving 100 mg of substance in a litre of water.

Phenitrothione was obtained by TLC isolation from Metatione E50. A sample of Metatione was diluted a hundred times with tetrachloromethane, and 5 μl of the solution was applied to a plate. A hexane–acetone mixture 5 : 1 was used for the elution. The spot of phenitrothione, detected with a UV lamp, was cut out and placed in a 25 ml volumetric flask. The substance was washed out with 1 ml of ethanol, and the supporting electrolyte of 0·05M-H_2SO_4 (pH 1·15) was added to give a solution containing phenitrothione in a concentration of 1·18 mg l^{-1}. This concentration was found polarographically using Dinobutone as standard, assuming that the diffusion coefficients of the two substances are nearly identical. Dinobutone also served to verify that no losses occur during the chromatographic separation). Solutions of lower concentrations were prepared by diluting with the supporting electrolyte. For a check, an analogous spot was cut out of a pure plate and handled in an identical manner.

Apparatus

The measurements were performed in a Kalousek's vessel with a thermostating jacket, interfaced to an LP 9 polarographic analyzer with a TZ 213 S recorder (Laboratorní přístroje, Prague). The electrode system was a combination of a mercury dropping electrode and a saturated calomel electrode. The chromatographic separations were carried out on Silufol UV 254 TLC plates (Kavalier, Votice) using 5 μl "Microcap" capillary pipets (Drummong Scientific, U. S.A.) and a mercury discharge tube with a 254 nm filter (Hanovia, Great Britain). A U 1 thermostat (Prüfgeräte-Werk Medingen) and an OP-8071 pH-meter (Radelkis, Budapest) were also used.

Polarographic Measurements

The dependences of the potentials and the peak heights and shapes on the composition of the supporting electrolyte were measured on solutions of DNOK, Dinobutone, and CDT in a concentration of 5 mg l^{-1} and on a solution of phenitrothione in a concentration of 1·18 mg l^{-1}. The concentration dependences of the peak heights were determined for DNOK and Dinobutone in a Britton–Robinson buffer pH 6·1 and for CDT and phenitrothione in 0·05M sulphuric acid. The concentration regions were 0·005—20 mg l^{-1} for DNOK and CDT, 0·025—20 mg l^{-1} for Dinobutone, and 0·006—2·36 mg l^{-1} for phenitrothione. The curves were recorded five times for each concentration and the limit of detection, limit of determination, correlation coefficient of the linear dependence, and the standard deviation of the determination were calculated.

The dependence of the polarographic current on the height of the mercury column was examined by the direct current polarography method. Measured were solutions of DNOK and Dinobutone ($\varrho = 1$ mg l^{-1}) in a supporting electrolyte of pH 6·1, CDT ($\varrho = 2$ mg l^{-1}) and phenitrothione ($\varrho = 1{\cdot}18$ mg l^{-1}) in a supporting electrolyte of pH 1·15.

The dependence of the polarographic peak height on temperature was investigated by the differential pulse polarography technique. The temperature was varied from 20 to 60°C in steps of 10°C.

For studying the possibility of determination of the pesticides in mixtures, solutions were made up containing the components in the same concentration, viz. $\varrho = 1$ mg l^{-1}; mixtures of DNOK, Dinobutone, and phenitrothione, and of DNOK, Dinobutone, and CDT in solutions of pH 1·15, 6·1, and 10·1 were measured by the DPP method.

RESULTS AND DISCUSSION

Effect of pH *of the supporting electrolyte*: The effect of pH on the potentials of the peaks for DNOK and Dinobutone is shown in Fig. 1. Only the two highest, well-deve-loped peaks were examined; in fact, a third, ill developed peak nine times lower than the highest one appears at more negative potentials for the two substances at pH 1·15–4·5. For DNOK, the second peak splits up in the alkaline region, pH

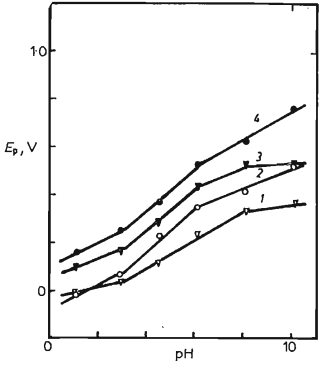

FIG. 1

Dependence of the potentials of the peaks of DNOK and Dinobutone on pH. *1*, *3* Dinobutone; *2*, *4* DNOK; *1*, *2* 1st peaks, *3*, *4* 2nd peaks; E_p peak potential. DPP technique, pulse amplitude 25 mV, drop time 2 s, depolarizer concentration 5 mg l^{-1}

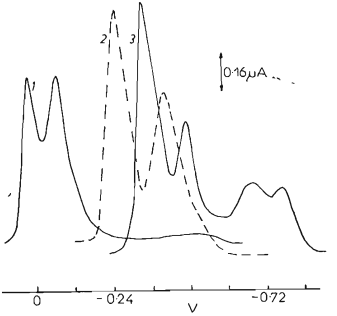

FIG. 2

Polarograms of Dinobutone at various pH values. *1* pH 1·15, *2* pH 6·1, *3* pH 10·1; E potential (S.C.E.); for the conditions see Fig. 1 caption

8·8–10·9; for Dinobutone the splitting is observed even in neutral solution and at pH 8·1 the two components are completely separated. Probably, in strongly alkaline solutions Dinobutone is hydrolyzed to give 2-(1-methylpropyl)-4,6-dinitrophenol, a substance differing from DNOK only in the size of the alkyl group in position 2 of the aromatic ring. This assumption is borne out by the identical positions of the three peaks in the polarograms of Dinobutone and DNOK at pH 10·1 ($E_{1/2}$ = = −0·531, −0·770, and −0·890 V). The most intense peak of Dinobutone ($E_{1/2}$ = = −0·360 V), however, remains in the polarogram even at this pH 10·1, indicating that the hydrolysis is highly incomplete. Polarograms of Dinobutone for the three pH values are shown in Fig. 2. The dependences of the peak potentials on pH for CDT and phenitrothione are depicted in Fig. 3. CDT in acid solution (pH 1·15) gives two well-resolved peaks, a sharp one at 0·00 V and a low and ill-developed one at −0·50 V; their height ratio is 5 : 1. The height of the second peak decreases with increasing pH and ultimately vanishes at pH 4·5, while the first peak shifts to negative potentials and splits up to form the third peak in Fig. 3. At pH 8·1, and additional peak appears at a potential more positive than the potentials of the two initial peaks (it is not shown in Fig. 3). Phenitrothione in the acid electrolyte (pH 1·15) affords a well-defined sharp peak at −0·085 V and another peak at −1·00 V. The potential of the second peak is pH-independent, its height is about six times lower than that of the first peak and diminishes with increasing pH to vanish at pH 8·1. The first peak splits up at pH < 2 and the two components are shifted to negative potentials with increasing pH.

The peak heights are highly dependent on pH and the composition of the solution

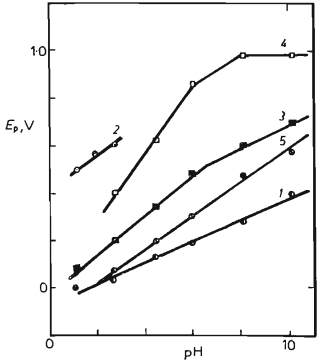

FIG. 3

Dependence of the potentials of the peaks of CDT and phenitrothione on pH. *1* CDT (1st peak), *2* CDT (3rd peak), *3* phenitrothione (1st peak), *4* phenitrothione (2nd peak), *5* CDT (2nd peak). For the conditions see Fig. 1 caption: concentrations of CDT and of phenitrothione 5 and 1·18 mg l^{-1}, respectively

for all of the pesticides examined. The height of the first peak of DNOK increases monotonically up to pH 8·1 and then remains virtually constant, while that of the second peak remains constant up to pH 8·1 and then decreases. For Dinobutone, the height of the first peak increases and that of the second peak decreases with increases pH over the region examined. For both substances, no major variations in the peak heights appear over the region of pH 4–8; a Britton–Robinson buffer with pH 6·1 was therefore selected for their quantitative determination. CDT and phenitrothione, on the other hand, are best determined in strongly acid solutions, in which they give rise to the maximum response; a 0·05M-H_2SO_4 solution, pH 1·15 was therefore chosen as the supporting electrolyte.

Polarographic behaviour of the pesticides. The mechanism of the electrode processes involved is rather complex. DNOK and Dinobutone have similar molecular structures. Their direct-current polarographic waves were recorded and the dependences of $\log [i/(i_d - i)]$ on E were evaluated. The slopes of these dependences indicate that the waves bear a pronounced irreversible character. This makes a conventional determination of the number of exchanged electrons impossible; the electrode reaction was therefore studied by comparing the polarograms of the two pesticides with those of nitrophenols, substances whose reduction mechanism has been investigated[1-3]. A polarographic analysis was carried out for 2-nitrophenol and 4-nitrophenol in a concentration of 5 mg l^{-1} in Britton–Robinson buffer pH 6·1. A single peak was observed in the DPP polarograms of the two substances at −0·39 and −0·50 V, respectively. In the same conditions, DNOK gave rise to two peak at −0·35 and −0·53 V; clearly, the former peak corresponds to the reduction of the nitro group in position 2, the latter corresponds to position 4. While an equimolar mixture of the two nitrophenols gives two peaks of identical intensity, the ratio of the peak heights for DNOK is 5·5 : 4. According to Chandra and Singh[1], 2- and 4-nitrophenol are reduced at pH 6·09 as far as the amines, with the exchange of six electrons. A six-electron reduction of these nitrophenols is reported also by Milner[2]. So it can be assumed that the two well-developed DPP peaks of DNOK in neutral solutions correspond to a consecutive reduction of the nitro groups, the peak at −0·35 V being due to the six-electron reduction of the nitro group in position 2 and the peak at −0·53 V being associated with the four-electron reduction of the nitro group in position 4. Very probably, the polarographic reduction of Dinobutone is alike; the positions of the two peaks are nearly identical with those of DNOK and the peak height ratio is 5·7 : 4.

The behaviour of CDT can be assumed to approach that of trifluoraline, from which it only differs by the substituent in position 1 of the benzene ring. Trifluoraline in strongly acid solutions is reported[1] to afford a single eight-electron wave; CDT at pH 1·15 also gives a sharp peak, at $E_{1/2}$ = 0·00 V, probably due to a simultaneous four-electron reduction of the two nitro groups to the hydroxylamine groups.

The polarographic behaviour of phenitrothione is comparable with that of parathione[3]; the relation between the peak height and the height of the mercury column, together with the temperature dependence of the peak height, indicates that the polarization curves of phenitrothione as well as of the other three pesticides bear an adsorption character.

Concentration dependence, detection limit, and precision of determination of the individual pesticides: The peak heights and peak areas were determined for DNOK. Dinobutone, 2-nitrophenol, and 4-nitrophenol, each in a concentration of 3·65 mol . l^{-1} at pH 6·1. Neither the peak heights nor the areas were found identical for the mutually corresponding peaks of the substances due to the differences in their diffusion coefficients; hence, individual calibration curves have to be plotted for the various pesticides. The concentration dependences of the current were measured in the concentration ranges of 0·02 – 20 mg l^{-1} for DNOK, Dinobutone, and CDT, and 0·02 – 2 mg l^{-1} for phenitrothione in the concentration region of 0·02 – 1 mg l^{-1} the dependences could be regarded linear for all of the substances, and the corresponding regression straigt line equations were calculated. The parameters are given in Table I; the correlation coefficients lay in the range of 0·9824 to 0·9999.

For the determination of the detection limits, the concentration dependences of the peak heights were followed in the regions of 0·005 – 0·1 mg l^{-1} for DNOK and CDT, 0·025 – 0·1 mg l^{-1} for Dinobutone, and 0·006 – 0·12 mg l^{-1} for phenitrothione. The limits of detection, c_d, and the limits of determination, c_q, were calculated according to Skogerboe and Grant[13]. The results are given in Table II along with the standard deviations for $n = 5$. As an illustration, Fig. 4 shows polarograms of DNOK for concentrations approaching the detection limit.

TABLE I

Coefficients of the regression straight lines $i_p = a + b\varrho$ for DNOK, Dinobutone, CDT, and phenitrothione

Depolarizer	Peak No	a μA	b μA l mg^{-1}
DNOK	1	0·010	0·664
DNOK	2	0·001	0·4631
Dinobutone	1	0·005	0·2437
Dinobutone	2	0·005	0·0998
CDT	1	0·020	0·5030
CDT	2	0·00001	0·0936
Phenitrothione	—	0·013	0·7653

Possibility of determination of the pesticides in mixtures: Although, strictly speaking, each pesticide calls for its own calibration plot, we sought whether some of the pesticides at least can be determined in their mixtures. Solutions were therefore prepared containing two or three nitro-pesticides in equal mass concentrations, and their polarograms were scanned at pH 1·15, 6·1, and 10·1.

TABLE II

Limits of detection c_d, limits of determination c_q, and standard deviations s (for $n = 5$) for the polarographic determination of DNOK, Dinobutone, CDT, and phenitrothione

Depolarizer	Peak No	c_d $\mu g\,l^{-1}$	c_q $\mu g\,l^{-1}$	s μA
DNOK	1	2·1	7·5	0·5648
DNOK	2	1·5	5·5	0·2796
Dinobutone	1	16·5	59·3	2·2531
Dinobutone	2	20·5	64·0	1·0426
CDT	1	2·6	9·4	0·7084
Phenitrothione	—	5·4	19·4	1·6166

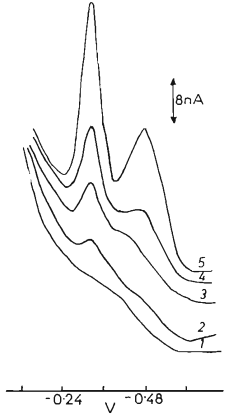

FIG. 4

Polarograms of DNOK for concentrations approaching the detection limit. Concentration in the supporting electrolyte ($\mu g\,l^{-1}$): *1* 0, *2* 5, *3* 10, *4* 20, *5* 50. *E* potential (S.C.E.), for the conditions see Fig. 1 caption

In the strongly acid solutions, the peaks overlapped considerably. In the neutral solutions, DNOK and CDT can be determined in their mixture – the content of CDT is determined from the height of the first peak, the content of DNOK, from the height of the third peak in the polarogram of the mixture. The second peak is an overlap of the second peak of CDT and the first peak of DNOK. In a mixture of three pesticides, DNOK, Dinobutone, and phenitrothione, in the neutral solvent, Dinobutone can be determined based on the height of the first peak ($E_{1/2} = -0{\cdot}24$ V), and DNOK, based on the height of the second peak ($E_{1/2} = -0{\cdot}36$ V). The second peaks of Dinobutone and DNOK and the first peak of phenitrothione merge to form the third peak in the polarogram. The second peak of phenitrothione affords the fourth peak of the mixture; it is ill-developed and unsuitable for analytical application.

In the alkaline region (pH 10·1), phenitrothione and Dinobutone can be determined in the presence of DNOK, Dinobutone from the height of the first peak at $-0{\cdot}33$ V, phenitrothione from the height of the third peak at $-0{\cdot}66$ V. The three remaining peaks are due to overlapping responses of the individual substances.

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