SOME REMARKS CONCERNING POLAROGRAPHIC DETERMINATION OF SULPHUR-CONTAINING HERBICIDES

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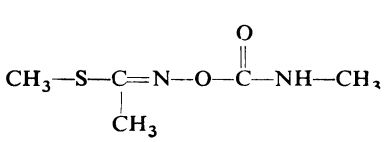
The herbicide methomyl (2-methylthio-propionaldehyde-*o*-methylcarbamoyloxime) can be determined using fast scan differential pulse voltammetry with hanging mercury drop electrode by the measurement of the peak at −1·30 V (S.C.E.) which is caused by the presence of methomyl in the ammoniacal buffer solution containing cobalt(II) salt. The peak current *vs* methomyl concentration dependence is linear over the concentration range 0·5 to 20·0 μg $.l^{-1}$. The herbicide aldicarb (2-methyl-2(methylthio)propionaldehyde-*o*-methylcarbamoyloxime) is determined by its influence on the differential pulse voltammetric curve of copper(II) recorded in electrochemically enriched solution in acidic medium. The corresponding peak current at the potential +0·08 V (S.C.E.) depends linearly on the aldicarb concentration in the range 0·07 to 5·00 μg ml^{-1}.

Modern electroanalytical methods play an important role in the determination of low amounts of organic substances[1]. In the case of sulphur containing agrochemicals the polarographic determination is usually based on the reduction of another function group which is present in the corresponding molecule (*e.g.* the reduction of —NO_2 group in the determination of parathion)[2]. The compounds containing —SH group are particularly suitable for polarographic determination because these compounds form insoluble complexes with mercury and can be thus determined by cathodic stripping voltammetry (CSV). When differential pulse mode is applied in these methods, the detection limit of μg l^{-1} can be reached[3]. In this paper are presented the results obtained in the study of the polarographic and voltammetric behaviour of the herbicides methomyl and aldicarb.

EXPERIMENTAL

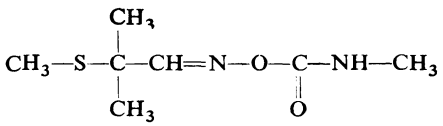
Chemicals and Apparatus

The studied herbicides were methomyl-2-methylthio-propionaldehyde-*o*-methylcarbamoyloxime



I

product of Dupont Co. (USA), 99·80%; and aldicarb (*II*) 2-methyl-2-(methylthio)propionaldehyde-*o*-methylcarbamoyloxime



II

product of Union Carbide Co., (USA), 99·90%. Both these chemicals were dissolved in water and 10^{-3} mol l^{-1} solutions were prepared. All chemicals used were of r.g., water was twice distilled in quartz apparatus.

Polarographic measurements were carried out with the Polarographic Analyzer PA-4 (Laboratorní přístroje, Prague). A three electrode system was used consisting of a Static Mercury Drop Electrode — S.M.D.E. 1 (Laboratorní přístroje, Prague) as the working electrode (in the mode of either dropping mercury electrode (D.M.E.) or hanging mercury drop electrode (H.M.D.E.), saturated calomel electrode (S.C.E.) as the reference electrode and platinum wire electrode as the auxiliary electrode. The pH values were measured with the pH meter PHM-25 (Radiometer, Denmark).

Methods

Besides *d.c.* polarography, differential pulse polarography (DPP) and normal pulse polarography (NPP) the method of fact scan differential pulse voltammetry (FSDPV) was used with the HMDE. This technique is a rapid version of DPP — five polarization pulses per second, pulse duration 100 ms, interval between pulses 100 ms, sampling identical as in commonly used DDP (ref.[4]). FSDPV was applied in anodic stripping voltammetry (ASV) and in voltammetric measurement in electrochemically enriched solution — a modification of ASV (ref.[5,6]) where after the electrolysis at the potential E_{el}, the potential of the HMDE is instantaneously switched to a more positive value — oxidation potential E_{ox}, and after an oxidation period t_{ox} the HMDE is polarized in the direction to more negative potential values.

RESULTS

No oxidation or reduction polarographic waves of both studied compounds were found in aqueous solutions in the pH interval 1—14. An indirect way of the determination based on the interactions of the studied compounds with metal ions was therefore examined.

Polarographic Behaviour of Methomyl in the Presence of Cobalt(II) *Ions*

It was observed that the presence of methomyl caused a somewhat similar effect as thiol or disulphide groups containing compounds in the medium of ammoniacal buffer containing cobalt(II) salt[7,8]. The sharp maximum on the d.c. wave of cobalt(II) complex decreased and became round after the addition of methomyl. This maximum was followed by a new wave with the half-wave potential −1·35 V (S.C.E.). Further

examination carried out with slower scan rate (1 mV s^{-1}) showed that in the presence of methomyl the existence of a prewave at the potential approx. 50 mV more positive than was the half-wave potential of the cobalt wave. Similar phenomena were observed when DPP was applied as the measuring technique. In this case the existence of a peak corresponding to the prewave was not distinguished only the widening of the cobalt peak was apparent.

When similar measurement were carried out using the HMDE following results were obtained. A prewave on the cobalt wave was distinguished at low polarization rates (2–10 mV s^{-1}) if *d.c.* technique was applied. Under these conditions the sum of the height of the prewave and of the cobalt wave increased linearly with increasing methomyl concentration. In differential measurement mode (DPP or FSDPP) this was evidently not valid. The peak corresponding to the *d.c.* wave with the half-wave potential −1·35 V is well developed and can be used analytically (Fig. 1). The peak current of this peak depends on the methomyl concentration and on the concentration of cobalt(II) salt. Maximum i_p values were obtained when cobalt(II) was present in ten to hundred molar excess with respect to the methomyl concentration. Under these conditions the i_p values depend also on the pH values of the supporting electrolyte. Above pH 10 and below pH 8 the mentioned peak was not recorded. The optimum buffer composition was the mixture of 0·05M-NH_3 and 0·05M-NH_4Cl, the current values were slightly influenced when the concentration of the buffer components was varied in the range from 0·01 to 0·1 mol/l. The described peak was also observed when 0·1M glycine buffer solution, pH 8·5 was used, no peak was recorded when ethylenediamine was applied as supporting electrolyte under otherwise identical conditions. If cobalt(II) was replaced by nickel(II) a peak at the potential approx. −1·30 V was also observed, the corresponding current was, however, lower than in the case of cobalt(II) salt. Under the optimum conditions (ammoniacal buffer solution, pH 8·5; hundred times molar concentration excess of cobalt(II) *vs* methomyl) the peak current depended linearly on methomyl concentration in the range 0·5 to 20·0 μg ml^{-1}, at higher methomyl concentration this dependence departured from linearity and reached a limit.

Normal pulse polarography (NPP) when applied for the examination of the influence of methomyl on the cobalt(II) wave in ammoniacal medium showed no effect

FIG. 1

Effect of methomyl on the FSDPV of cobalt in ammoniacal medium. *1* 0·05M ammoniacal buffer, pH 9·1; cobalt conc. 2 . 10^{-4} mol l^{-1}; *2* as curve *1*, methomyl conc. 1 . 10^{-5} mol . l^{-1}. HMDE

when DME was used as working electrode. If, on the other hand, the HDME was used a new wave with a maximum ($E_{1/2}$ = −1·60 V) appeared on the NP polarogram when the initial potential (−0·50 to −0·20 V) was applied, the height of the more negative wave rapidly decreased and this wave shifted to more positive potential. Simultaneously a prewave on the cobalt(II) wave was recorded under these conditions.

Simultaneously a new wave appeared with the half wave potential 200 mV more negative than that of the cobalt wave, the heights of the both waves were practically identical (Fig. 2).

Polarographic Behaviour of Aldicarb in the Presence of Copper(II) *Ions*

Polarographic behaviour of aldicarb was examined in an identical way as that of methomyl. It was found that aldicarb had no effect on the polarographic reduction of cobalt(II) in ammoniacal medium. It was, on the other hand, observed that this compound influenced the ASV peak of copper(II) in acidic medium – a new sharp peak appeared on the stripping voltammogram of copper. This effect was more pronounced, when instead of ASV the technique of electrochemical enrichment was applied. If copper was determined using this technique in acidic medium (mixture of 0·1M-$NaClO_4$ and 0·01M-$HClO_4$) the peak potential of copper(II) was +0·02 V. In the presence of aldicarb a new sharp peak with the E_p value +0·08 V was formed (Fig. 3). The peak current of the peak at +0·08 V depended on the electrolysis time, t_{el}, duration of the rest period t_R, and on the oxidation period t_{ox}; the corresponding

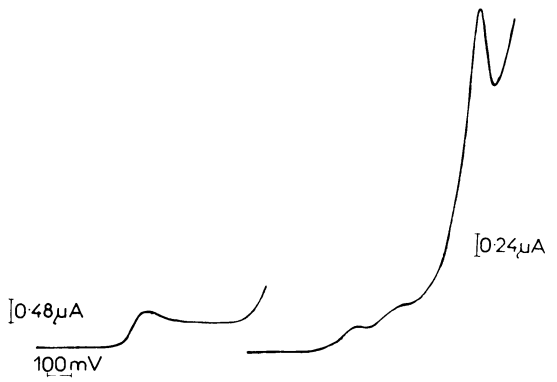


FIG. 2

Effect of methomyl on NPV of cobalt in ammoniacal medium. *1* 0·05M ammoniacal buffer, pH 9·1; cobalt conc. 2 . 10^{-4} mol l^{-1}; *2* as curve *1*, methomyl conc. 1 . 10^{-5} mol l^{-1}; initial potential: −0·60 V, HMDE

dependences are shown on Fig. 4. The described effect of aldicarb was observed under the conditions, when copper(II) was kept at the concentration level 10^{-6} mol . $.1^{-1}$ while the aldicarb concentration was varied in the range 10^{-7} to 10^{-5} mol l^{-1}. The peak current of the newly formed peak depends also on the polarization rate. While the peak current of copper (+0·02 V) increased with increasing polarization rate (in the range 2–20 mV s^{-1}), the peak current of the peak at +0·08 V slowly increased in the interval 2–10 mV s^{-1} and decreased above the polarization rate 10 mV s^{-1}. The peak current of this peak depends linearly on the aldicarb concentration in the range from 4 . 10^{-7} to 6 . 10^{-5} mol l^{-1}.

In direct FSDPV carried out with HMDE the presence of aldicarb caused only a slight increase of the height of the copper peak. This increase did not depend

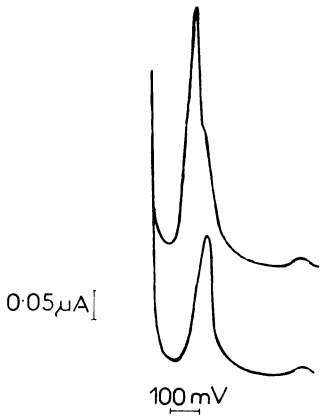


FIG. 3

Effect of aldicarb on the FSDPV peak of copper recorded using the method of electrochemical enrichment. *1* the upper curve 6 . 10^{-6} mol l^{-1} copper in 0·1M-$NaClO_4$ + + 0·01M-$HClO_4$; E_{el} −0·90 V; E_{ox} +0·20 V; t_{el} 30 s, t_R 60 s; t_{ox} 5 s; *2* the lower curve as curve *1*, aldicarb conc. 1·2 . 10^{-5} mol l^{-1}, HDME

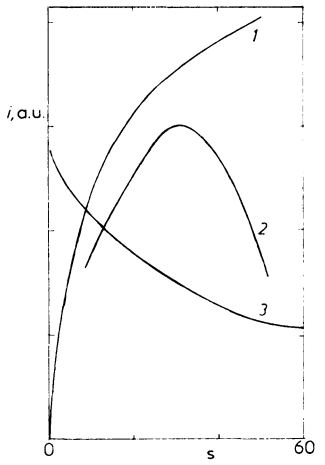


FIG. 4

Dependence of the anomalous current (*i*, arbitrary units) caused by aldicarb on the parameters of the electrochemical enrichment method in copper determination. 4 . 10^{-6} mol l^{-1} copper and 1·2 . 10^{-5} mol l^{-1} aldicarb in 0·1M-$NaClO_4$ + 0·01M-$HClO_4$; E_{el} −0·90 V, E_{ox} +0·25 V; *1* dependence on the duration of the oxidation time at t_{el} 30 s and t_R 30 s; *2* dependence on the duration on the electrolysis time at t_R 15 s and t_{ox} 5 s; *3* dependence on the duration of the rest period at t_{el} 30 s and t_{ox} 5 s

linearly on aldicarb concentration and was observed only over a short concentration interval from $4 . 10^{-6}$ to $1 . 10^{-5}$ mol l^{-1}.

DISCUSSION

As follows from the results given above the effects caused by the studied compounds are similar to the effects of thiol or disulphide groups containing compounds, which influence the polarographic behaviour of cobalt(II) in ammoniacal medium[7] or stripping of copper in acidic media[8]. In the first case the thiol or disulphide groups compounds exert catalytic effect upon hydrogen evolution, in the second case the effect is caused by the formation of mercury and copper complexes and their adsorption on the surface of the mercury electrode. The results presented here cannot be explained in such a way. In the case of the effect of aldicarb which does not form an insoluble compound or complex with mercury but which is adsorbed in a wide potential range on the surface of the mercury electrode the following proposal can be postulated: If copper is deposited on the HMDE by electrolysis then after the potential of the HMDE is switched to a positive value copper in the amalgam is oxidized and forms an adsorbing copper complex with aldicarb.

The adsorbed complex is reduced with less energy than the metal ions in the solution and thus a sharp peak appears at the potential more positive than that of copper(II). The observed experimental data are in agreement with this proposal: When in the described measurement mode the rest period t_R was prolonged keeping the electrolysis and oxidation time constant, the peak current increased (Fig. 4). During the prolonged rest period aldicarb is adsorbed and thus higher amount of aldicarb can be consumed for the formation of the complex after the electrode potential is switched to positive value. On the other hand when the electrolysis time was prolonged under otherwise identical conditions, the peak current decreased when a certain value of the electrolysis time was reached (Fig 4). Under these conditions the amount of aldicarb is not sufficient for that of cupric ions (formed at positive potential) to enable the course of the proposed process. When the oxidation time was prolonged the peak current decreased but much slower than the peak current of copper(II) ions recorded in the absence of aldicarb. This shows that the diffusion of the copper complex from the electrode is retarded by adsorption. Similarly the results with varied scan rate show that when low scan rate is applied, higher amount of the complex can be adsorbed and on the contrary the application of higher rates results in the decrease of the adsorbed complex.

In the case of the effect of methomyl on the reduction of cobalt ammonia complex, the results of the normal pulse measurement with HMDE show the evidence of potential dependent adsorption. Some of the dependences observed (dependence of the anomalous current on pH, cobalt concentration, buffer quality and concentration) are similar to that reported for the catalytic hydrogen evolution caused *e.g.* by cys-

teine in cobalt ammoniacal solutions. In spite of these similarities an explanation of such mechanism where methomyl is involved cannot be, however, given because the source of hydrogen (as is the sulphydryl group in the described systems) is not known.

From the analytical point of view most important is that both compounds – methomyl and aldicarb – although structurally very closely related can be distinguished and determined with sufficient sensitivity using the described voltammetric techniques in combination with HMDE.

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