Reductive deactivation of some *s*-triazine herbicides: prometryne, desmetryne and terbutryne

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The electrochemical behaviour (DC and DP polarography) of the methylthio-bis(alkylamino) *s*-triazine herbicides prometryne, desmetryne and terbutryne on mercury electrodes has been studied in the acidity range 2.25 M H_2SO_4 to pH 6.5. Two two-electron irreversible reduction processes were found, complicated with adsorption. At pH values higher than the protonation p*K* of the triazine ring (*ca.* 4), this protonation reaction preceded the reduction processes. Reduction mechanisms are proposed for pH < p*K* and pH > p*K*. The products obtained in the electroreduction of dilute solutions of the above herbicides show a lower toxicological effect than that of the original compounds (lower aromatic character and cleavage of the –SCH_3 group). Thus, electrochemical deactivation at pH ≤ 3.5 and at potentials around –1.10 V (*vs.* the Ag/AgCl/KCl$_{sat}$ electrode) can be a valid method to deactivate these molecules. Finally, the reductive route can be an alternative environmental degradative process in waters under strong reductive conditions, with pH values equal or lower than 3.5 pH-units, and rich in carbonaceous materials on clays. In these ambients oxidative photolytic detoxification of herbicides cannot occur.

Keywords: DC and DP polarography, prometryne, desmetryne, terbutryne, triazine herbicides.

INTRODUCTION

The 2-methylthio-4,6-bis(alkylamino)-1,3,5-triazines, prometryne, desmetryne and terbutryne (widely used in agriculture from the 1950's) are white crystalline solids, slightly soluble in water, having p*K* values of the N5 ring nitrogen of around 4 in aqueous solution. This implies that above pH 4 the unprotonated forms of the compounds predominate in solution. Scheme 1 shows the structures of the three studied substances.

The *s*-triazines are chemicals with persistence in soils and hydric sediments, showing half-lifes of the order of months, due to their low solubilities in water, and to their strong sorption on carbonous materials and clays.[1] This can be the origin of important environmental and toxicological problems because these compounds can be bioaccumulated

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Prometryne   Desmetryne   Terbutryne
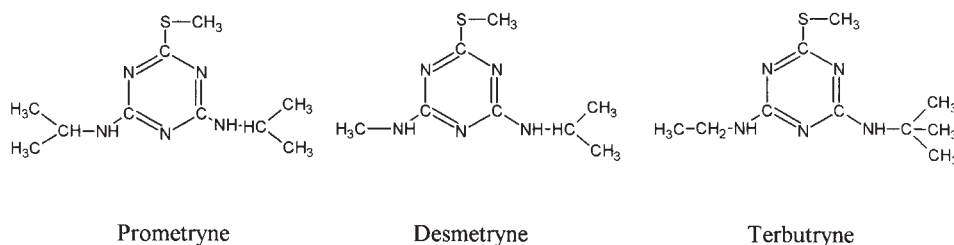
Scheme 1.

along the trophic chain, especially in fruits and oils, and finally, in humans. Triazines are, generally, selective pre- and post-emergence herbicides without hormonal activity and which allow seed germination. Their herbicidal action comes from a reduction in the yield of photosynthesis in herbicide-affected plants.[2] Furthermore, triazines are degraded by oxidative photolysis and microbial action in soils.[3]

Chlorinated triazine herbicides are usual pollutants, being detected in appreciable concentrations in waters.[4–7] Thus, concentrations ranging from more than 1 μg/l of atrazine, diethylatrazine and deisopropylatrazine, up to levels lower than 0.05 μg/l of propazine, prometryne and other alkyl derivatives can be detected in the river waters of the USA and Europe.

The laboratory degradation of such herbicides by ozonization,[8] UV degradation catalyzed by TiO_2[9] and chemical oxidation,[10,11] has been studied. These studies showed that OH· radicals were essential in the alkylation of the triazinic ring. The degradation of these chemicals in the environment is mainly photochemical yielding alkyl derivatives probably *via* the formation of hydroxyatrazines.[12]

Some studies reported the use of different electrochemical techniques for the determination of such herbicides[13–20] and the reductive cleavage of the Cl atom or the –SCH$_3$ group was proposed. Skopalová and Kotoucek[21] found that only the protonated form of the herbicide was reduced in two consecutive two-electron reactions: the reduction of the triazine ring yielding an unstable intermediate, which loses a HCl molecule, and reduction of the ring in the 3–4 or 4–5 position. This mechanism was also essentially proposed by Pospisil *et al.*[22] for the electroreduction of atrazine and terbutylazine on mercury electrodes. At pH > p*K* these authors concluded that both compounds were adsorbed on the electrode surface.[23] Recently, Skopalová *et al.*[24] examined the electroreduction of prometryne and related methylthio-*s*-triazine herbicides finding that 4,6-bis(isopropylamino)-1,3,5-triazine is formed as an intermediate of the reduction, the end product being the protonated dihydro-4,6-bis(isopropylamino)-1,3,5-triazine. The electrochemical reduction of hexazinone (3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1*H*, 3*H*-dione)) was examined[25] and the reductive cleavage of dimethylamine followed by the two-electron reduction of the de-aminated compound was proposed.

In all the cases, the products of the electrochemical reduction of triazines had a lower toxicological action than the original compounds, because of the known fact that heteroaromatics have more marked carcinogenic, teratogenic and toxicological properties than those of the equivalent non-aromatic compounds; in addition, the loss of the chlorine atom implies a lower toxicity compared to the chlorinated molecules.[3,26]

In previous works carried out in our laboratory, the electrochemical reductions of simazine and propazine on mercury electrodes were studied,[3,27,28] finding that the above proposed reaction scheme is essentially followed. The processes involve the uptake of four electrons and one (pH < 1.7) or two (pH > 1.7) H^+ ions per herbicide molecule yielding non-aromatic and non-chlorinated final products. Linear-sweep voltammetry showed that both the protonated and unprotonated forms of simazine are highly adsorbed on the electrode.[3,28]

According to the above, the reductive mechanism could constitute a possible reductive degradation route on the laboratory and the industrial scale, as well as in a few specific natural aquatic environments where the mechanism of oxidative photolytic detoxification does not act, as for example: (a) waters under strong reductive conditions associated to very poor or the absence of oxygenation, *i.e.,* deep underground anaerobic waters, and deep waters of lakes and oceans rich in suspended matter; (b) very acidic waters with pH < 4.0, *i.e.,* those of the volcanic lakes of Japan, and some undergound acidic waters with very low capacity of renovation (non-amountable flows).[3]

Finally, the electrochemical detoxification of simazine- and/or propazine-polluted waters could be carried out by adjusting the pH of the medium to a value lower than 4 on both the laboratory-scale and the industrial-scale and operating at potential values around –1.00 V (referred to the Ag/AgCl/KCl$_{sat}$ electrode). Also, the presence of suspended materials (organic and/or inorganic, natural or induced) should favour this reduction because of the high adsorption capacity of the herbicides on these substrates.

The reduction of the methylthio derivatives was assumed to follow the same mechanism as those corresponding to the chloro derivatives.[18–24] However, some experimental results have led to the thought that there are differences in the electrochemical behaviour that cannot be explained by that reaction pathway. Following the line of investigation developed in our laboratory and related with the electrochemical study of the deactivation of substances of interest as environmental pollutants, such as pyrithione[29,30] simazine[3] and propazine,[3] the aim of this work was to contribute to the elucidation of the electrochemical reduction mechanism of the 2-methylthio-4,6-bis(alkylamino)-1,3,5-triazines, prometryne, desmetryne and terbutryne on mercury electrodes, as well as the possible environmental implication of the above. The electrochemical reductive pathway, similar to the cases of simazine and propazine, could be a possible reductive degradation route of these derivative-triazines on both the laboratory and industrial scale, at the same time to be operative in a few specific natural aquatic environments where the mechanism of oxidative photolytic detoxification does not occur.

EXPERIMENTAL

All the reagents used were of Merck analytical grade with the exception of the three herbicides, which were from Polyscience (HPLC standard quality). They were used without further purification. The working concentrations of herbicides in both DP and DC polarography were usually 1.00×10^{-4} M, 2.00×10^{-4} M and 1.00×10^{-4} M for prometryne, desmetryne and terbutryne, respectively. The concentration was evidently changed in those experiments in which the influence of this variable was studied.

Solution of sulfuric acid, for pH < 1.2, and 0.1 M in both acetic and phosphoric acids for 2 < pH < 7, were used as the supporting electrolytes. Stock solutions of prometryne, and terbutryne were prepared in pure ethanol and stored in the dark at 277.0 ± 0.1 K to avoid decomposition. The measurements were performed in

media containing 1–2 % ethanol. The ionic strength was adjusted to 0.3 M with solid NaCl and the pH was adjusted with solid NaOH. All solutions were purged with purified nitrogen before the polarography measurements and the temperature was kept at 298.0 ± 0.1 K. Moreover, all potentials were measured against the Ag/AgCl/KCl$_{sat}$ electrode.

On the other hand, DP and DC polarographic measurements were made using a computerized electrochemical system CAEM model SEA-1210. The working electrode was a Metrohm 6-1220.000 capillary. Triply distilled mercury was used. The dropping time was 1 s and the scan rate was 2 mV s^{-1}. For DP polarography, the pulse amplitude was –15 mV and the pulse duration was 50 ms. Finally, the DP polarograms were analyzed using a curve-fitting method and previously described equations.[31]

RESULTS AND DISCUSSION

Electrochemical reduction on the laboratory-scale

The polarographic reduction of prometryne, desmetryne and terbutryne in the acidity range 2.25 M H$_2$SO$_4$ to pH 6 (2 % by volume of ethanol in the solution for terbutryne to ensure solubility) shows a single distorted wave in both DC and DP polarography. This wave decreased in intensity and disappeared above pH 5–6. Due to the strong distortion observed in all cases in the rising part of the DC polarograms which hinders their exhaustive analysis, the mechanistic conclusions given in this paper are supported mainly by the DP polarographic results.

The DP polarograms were analysed using the equation corresponding to a first-order process.[31] Over the entire pH range studied, the DP polarograms can be deconvoluted into three peaks, which will be labeled as 1, 2 and 3 following the increasing order in the negative potential at which they appear (see Fig. 1). Peaks 2 and 3 showed intensities much greater than peak 1, and are the main reduction peaks as will be shown in this discussion. All the peaks were shifted towards more negative potentials as the pH was increased.

The peak currents, I_p, varied with the pH of the medium, having maximum (and roughly pH-independent) values below *ca.* pH 3.5. They decreased on increasing the pH above 3.5 and finally disappeared above pH 6. The highest I_p value corresponded to peak 2. That presented by peak 1 was much lower at high concentration values but of the same order as that of peak 3 at low concentration values.

The "b" values (a parameter obtained from the equations of the waves and the characteristic of each type of reduction process) of the peaks were also obtained by curve fitting. For the main peaks, the mean "b" values changed gradually from around 30 mV at pH < 2.5 to *ca.* 40 mV at pH > 4.5–5, whereas the "b" values corresponding to peak 1 were always around 40 mV (slightly higher at high pH values).

On the other hand, the parameter that depends on the concentration in DP polarography is the peak area which is similar to the limiting current in DC polarography and is proportional to the product "$I_p b$" for first-order processes.[28,31] In this way, the evolution of these products with pH is very similar for the three compounds studied, but the individual values of the areas of peaks 2 and 3 are different for each herbicide. To explore the relation between peak 1 and peaks 2 and 3, the dependence of the peak areas with the reactant concentration was investigated as is shown in Fig. 2.
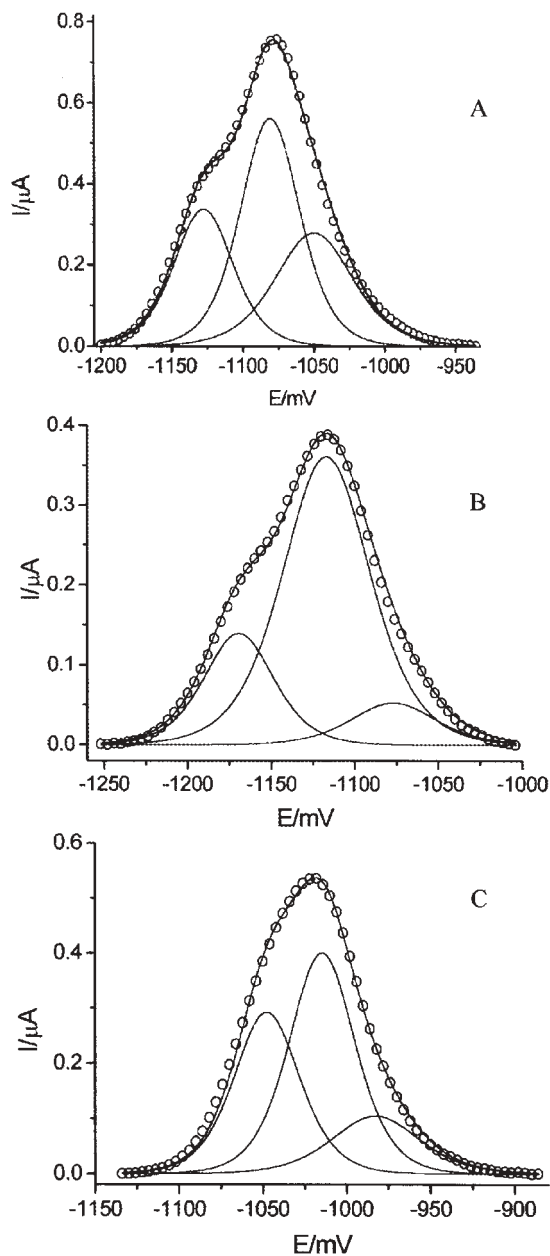
Fig. 1. Deconvolution of the DP polarograms of herbicides obtained by subtracting the DP polarograms in the presence and in the absence of reactant: (O)experimental data; (——) theoretical values. (A) Prometryne 2×10^{-4} M, pH 1.6; (B) Desmetryne 1×10^{-4} M, pH 3.6; (C) Terbutryne 1.2×10^{-4} M, pH 2.4.

As can be seen, the peak area of peak 1 remained unchanged when the herbicide concentration was increased up to values of 10^{-3} M for prometryne and 5.0×10^{-4} M for desmetryne and terbutryne. The peak areas of peaks 2 and 3 were very roughly proportional to this variable, at least at low concentration values: linearity of peak areas *vs. c* was clear up to concentrations of 5×10^{-4} M prometryne, and 2.5×10^{-4} M desmetryne and
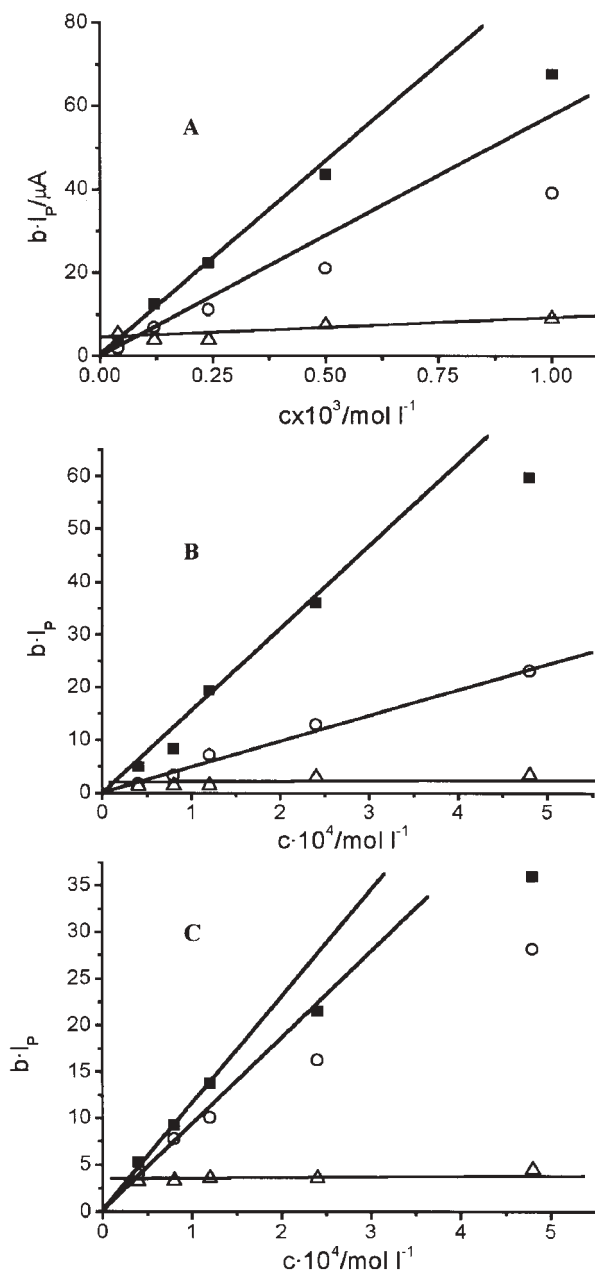
Fig. 2. DP polarography. Dependence of the peak areas (through "bI_P") on the herbicide concentration, at pH 2.0 (Δ)peak 1; (O)peak 2; ($\blacksquare$)peak 3. (A) Prometryne; (B) Desmetryne; (C) Terbutryne.

terbutryne. In addition, the dependence of the limiting current, i_L, in DC polarography with the reactant concentration was very similar to that observed for peaks 2 and 3. The above behaviour implies that peaks 1 correspond to adsorption phenomena, these results being very similar to those obtained for chlorinated derivatives.[27,28]
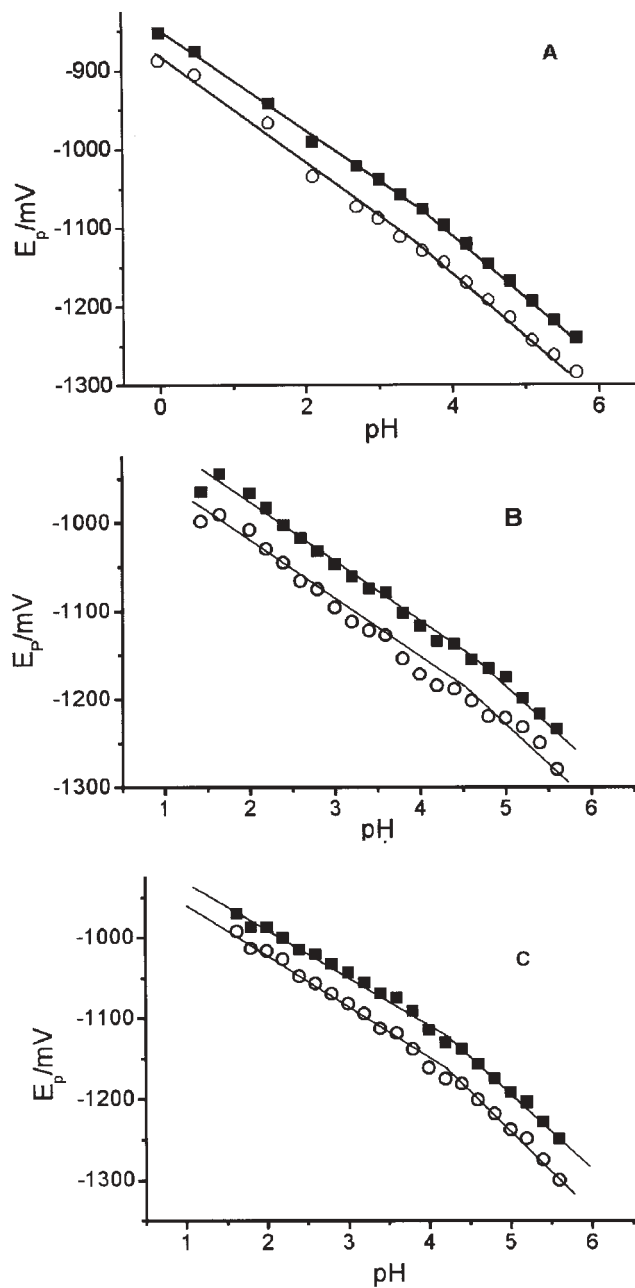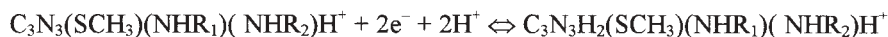
Fig. 3. DP polarography. Dependence of the peak potentials of peak 2 (squares) and peak 3 (circles) on pH. (A) Prometryne 1.0×10^{-4} M; (B) Desmetryne 2.0×10^{-4} M; (C) Terbutryne 1.0×10^{-4} M.

The overall number of electrons involved in the reduction process was four as was confirmed by comparing the DC polarograms with those corresponding to the reductions of simazine and propazine under similar conditions.[19,20,27,28] Moreover, the constant potential coulometric analysis of the reduction of prometryne[24] corresponded to the exchange
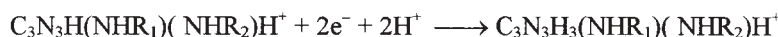
of $4.36 \pm 0.59\ F\,\text{mol}^{-1}$. The relative values of the areas of peaks 2 and 3 indicate that these peaks must correspond to first-order two-electron reduction processes only at the highest pH values, *i.e.*, at pH values greater than the protonation pK of the pyridine ring, being the main mass transport due to diffusion.

Nevertheless, at very low pH values, the peaks 2 have an area greater than that corresponding to a two-electron process and, at the same time, the area of peak 3 is less than that corresponding to a two-electron process. By comparing this behaviour with that of propazine (both molecules differ only in the groups at the position 2, which are –Cl and –SCH$_3$ respectively), it can be concluded that the intermediate obtained after the two first electronic uptakes is different in the two cases. Moreover, the decrease of the area of peak 3 when the acidity of the medium is increased, accompanied by the parallel increase in the area of the peak 2, suggests that the species reduced at the potentials of peak 3 is involved in a chemical reaction. Since the decrease of peak 3 is not mirrored in the parallel appearance of a new peak, but in the parallel increase of peak 2, the other species involved in such a chemical reaction must be totally (and quickly) reduced at the potentials of peak 2, and it could be the above-mentioned 4,6-bis(isopropylamino)-1,3,5-triazine.

Taking into account the evolution of the peak potentials obtained (see Fig. 3), and that of the peak intensities with pH and herbicide concentration, as well as other electrochemical parameters, and regarding the reported electrochemistry of the chlorinated triazines, the electroreduction of the herbicides at pH < pK must correspond to the processes shown in Scheme 2.

$$C_3N_3(SCH_3)(NHR_1)(NHR_2)H^+ + 2e^- + 2H^+ \Leftrightarrow C_3N_3H_2(SCH_3)(NHR_1)(NHR_2)H^+$$

$$C_3N_3H_2(SCH_3)(NHR_1)(NHR_2)H^+ \Leftrightarrow C_3N_3H(NHR_1)(NHR_2)H^+ + CH_3SH$$

(a)

$$C_3N_3H(NHR_1)(NHR_2)H^+ + 2e^- + 2H^+ \longrightarrow C_3N_3H_3(NHR_1)(NHR_2)H^+$$

(b)

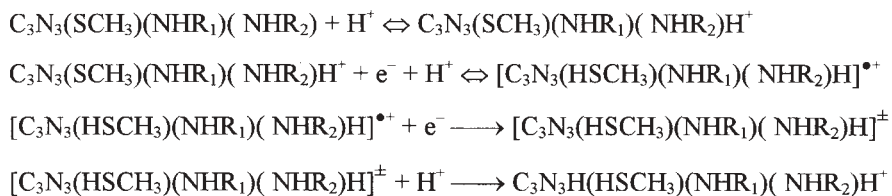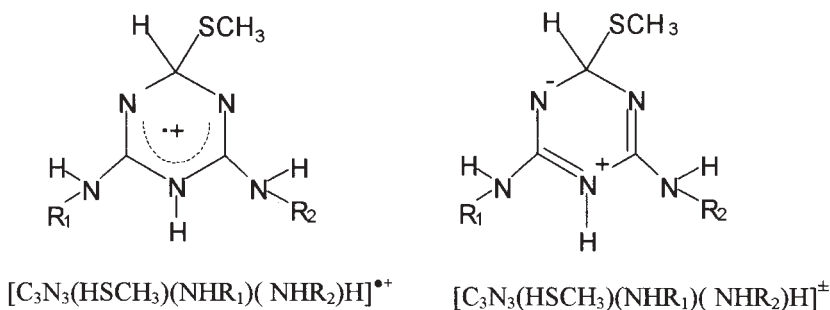$$C_3N_3H_2(SCH_3)(NHR_1)(NHR_2)H^+ + 2e^- + H^+ \longrightarrow C_3N_3H_3(NHR_1)(NHR_2)H^+ + CH_3SH$$

Scheme 2.

The experimental results agree with the theoretical predictions based on the reaction scheme, in the most acidic media. Thus, theoretical predictions indicate that the variation with pH of the peak potentials of peaks 2 and 3 must be linear having a common value of the slope of $-2.303RT/F$, that at 298 K is around –60 mV per pH unit. The dependences of the peak potentials with the pH are shown in Fig. 3, and two linear segments can be observed for peaks 2 and 3, at pH values lower and higher than *ca.* 4. The slopes of these lines were around -62 ± 4 mV decade^{-1} and -79 ± 3 mV decade^{-1}, for both peaks, in agreement with those expected theoretically. Also, the plots of $E_{1/2}$ *vs.* pH showed two roughly linear segments with slopes
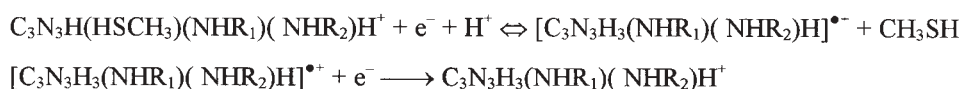
Peak 2

$$C_3N_3(SCH_3)(NHR_1)(NHR_2) + H^+ \Leftrightarrow C_3N_3(SCH_3)(NHR_1)(NHR_2)H^+$$

$$C_3N_3(SCH_3)(NHR_1)(NHR_2)H^+ + e^- + H^+ \Leftrightarrow [C_3N_3(HSCH_3)(NHR_1)(NHR_2)H]^{\bullet+}$$

$$[C_3N_3(HSCH_3)(NHR_1)(NHR_2)H]^{\bullet+} + e^- \longrightarrow [C_3N_3(HSCH_3)(NHR_1)(NHR_2)H]^{\pm}$$

$$[C_3N_3(HSCH_3)(NHR_1)(NHR_2)H]^{\pm} + H^+ \longrightarrow C_3N_3H(HSCH_3)(NHR_1)(NHR_2)H^+$$

with

$$[C_3N_3(HSCH_3)(NHR_1)(NHR_2)H]^{\bullet+} \qquad [C_3N_3(HSCH_3)(NHR_1)(NHR_2)H]^{\pm}$$

Peak 3

$$C_3N_3H(HSCH_3)(NHR_1)(NHR_2)H^+ + e^- + H^+ \Leftrightarrow [C_3N_3H_3(NHR_1)(NHR_2)H]^{\bullet-} + CH_3SH$$

$$[C_3N_3H_3(NHR_1)(NHR_2)H]^{\bullet+} + e^- \longrightarrow C_3N_3H_3(NHR_1)(NHR_2)H^+$$

Scheme 3.

around –63 and –80 mV per pH unit, in agreement with the values of –56 and –76 mV per pH unit reported[19] for the $E_{1/2}$ of prometryne at high concentrations. These values can be considered as a combination of the half-wave potentials of the two main reduction waves, since these are displaced by the same amount with a change of pH.

On the other hand, the observed decrease with pH in both i_L and the overall DP peak area at pH > 4 resembles an acid-base dissociation curve. This fact indicates that a protonation reaction prior to the electrode process limits the reduction rate. The species in the solution at these pH values is the unprotonated herbicide, whereas the species reduced at the electrode is the protonated one. Thus, the decrease of the limiting and peak currents with pH due to the protonation of the herbicide can be described by the well-known Koutecky equation.[32] Moreover, due to fact that the electrochemical reaction order with respect to the H$^+$ ion is 2 and that the dependence of E_p with the pH is around –80 mV per

pH unit, and of the Tafel slopes values, the reaction schemes for the higher pH values must correspond to Scheme 3 for peaks 2 and 3.

Environmental and toxicological considerations

The reduction of the three herbicides studied needs a total of four electrons per molecule of reactant and must be conducted, preferentially, at pH < 3.5. This process could be used in the treatment of prometryne-, desmetryne- and/or terbutryne-polluted industrial or waste waters prior to being discharged to natural hydric environments, if the products obtained after the electroreduction have a lower toxicity than that of the original herbicide.

In this way, it must be noted that all the final products produced by the electroreduction processes of the herbicides must effectively have lower toxicological activity than that of the original compounds: the products have a less aromatic character than the starting compounds. The above assumption is supported by the known fact that heteroaromatics have more marked carcinogenic, teratogenic and toxicological properties than the equivalent non-aromatic compounds.[3,26] In addition, the cleavage of the group $-SCH_3$ of the herbicides must also imply a lower toxicity of the electroreduced herbicides compared with the non-electroreduced ones. So, the electroreduction of dilute solutions of prometryne (5×10^{-4} M), and desmetryne and terbutryne (2.5×10^{-4} M) at pH-values 3.5 or lower operating at potential values around -1.10 V (against the $Ag/AgCl/KCl_{sat}$ electrode) can be a valid method of deactivating these molecules. Also, the electrochemical process can act on both dissolved substance and adsorbed substance.

On the other hand, due to the potential negative environmental effect linked to the mercury electrodes, new experiments are being performed in which other electrodes, such as carbon and platinum, are applied for the electrochemical reductive deactivation of solutions of prometryne, desmetryne and/or terbutryne. Furthermore, the use of a carbon electrode with an electrodeposited thin layer of mercury (a few atoms of thickness) reduces drastically the amount of mercury used in the process.[3,31,33]

И З В О Д

РЕДУКТИВНА ДЕАКТИВАЦИЈА НЕКИХ ХЕРБИЦИДА НА БАЗИ *s*-ТРИАЗИНА: ПРОМЕТРИН, ДЕСМЕТРИН И ТЕРБУТРИН

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Проучавано је електрохемијско понашање (DC и DP поларографија) прометрина, десметрина и тербутрина (метилтио-бис(алкиламино) *s*-триазинских хербицида) на живиној електроди у сумпорној киселини у области pH 2,25–6,5. Уочене су две иреверзибилне двоелектронске редукције, праћене адсорпцијом. При pH вредностима већим од p*K* протонације триазинског прстена (око 4) ова реакција протонације претходи процесу редукције. Предло-

жени су механизми реакције при pH < pK и при pH > pK. Производи електроредукције разблажених раствора ових хербицида имају мањи токсиколошки ефекат од полазних једи-њења (мањи ароматични карактер и отцепљивање –SCH$_3$ групе). Према томе, електрохе-мијска редукција при pH ≤ 3,5 и при потенцијалима око –1,10 V (*vs.* Ag/AgCl, KCl$_{sat}$) може бити добра метода за деактивацију ових молекула. Најзад, редукција може бити алтернативан деградациони процес у природи у води у јачим редукционим условима, при pH ≤ 3,5 и у присуству карбонизованих материјала у глини. У таквим условима оксидативна фотолитичка детоксификација не може да се одиграва.

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