Journal of Applied Electrochemistry (2006) 36:635–642
DOI 10.1007/s10800-006-9115-1

Reaction pathways in the electrochemical degradation of thiocarbamate herbicides in NaCl solution

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Received 8 April 2005; accepted in revised form 22 December 2005

Key words: degradation, electrolysis, end products, intermediates, reactions, thiocarbamates

Abstract

We have identified the intermediates and end products which are formed during the electrolytic degradation of thiocarbamate pesticides in aqueous NaCl solutions and investigated how the intermediate and end product volumes and ratios depend on reaction conditions. Further, we have defined both the reaction pathways leading to intermediate and end product formation and the methods affecting this process. The degradation of the molecular part containing the N atom is accounted for, as are the listed reactions and reaction pathways that affect degradation. If pH is changed, the ratio of degradation products NO_3^- and N_2 can be influenced in favour of N_2 gas. This pH change can then be produced without additional material by changing the construction of an electroflotation cell. To implement degradation, "flotation electrolysis" has been found to be an effective method as it facilitates a regulated pH-shift, foam handling and gas bubble rising velocity. The efficiency of the method can be further enhanced by UV photolysis.

1. Introduction

In industry, thiocarbamate herbicides (EPTC, Vernolate, Molinate, Cycloate, Butylate) are commonly produced through a N-acylising reaction, where amine surplus and NaOH acid acceptors are applied in stoichiometric amount to bring the reaction to completion. As a result, the wastewater contains both organic and inorganic (8–22 w/w% NaCl) pollutants [1, 2]. Every year several thousand cubic meters of such wastewater can be produced [2, 3].

It is well known that the NaCl content of aqueous solutions can be reduced through electrolysis. This happens in the industrial production of Cl_2 and NaOH. However, aqueous NaCl solutions contaminated with organic materials, e.g. with thiocarbamates, cannot undergo NaCl electrolysis without treatment. From the organic pollutants containing N atoms, e.g. from amines, chloramines may be produced, causing operational breakdown or even explosion [4]. Therefore, thiocarbamate pollutants should be degraded in such a way that no dangerous substances like NCl_3 intermediates are formed or retained in treated wastewater.

The exact mechanism of the electrochemical degradation of thiocarbamates in NaCl solution is unknown; neither has there been any investigation so far into the electrochemical degradation of secondary amines, which comprise part of the thiocarbamate molecule containing N atoms. On the other hand, the anodic oxidation of primary aliphatic amines and the anodic oxidation of primary, secondary and tertiary alphatic amines have been investigated [5]. It was found that the manner of degradation is in many respects similar to the mechanism hypothesised by Wei and Stewart for alkali permanganate oxidation of primary amines [6].

Wei and Stuart are of the opinion that the reaction starts with the loss of electrons from the N atom. An iminium radical cation is produced, which is then further oxidised and degrades into ammonium and aldehyde through hydrolysis. This mechanism is similar to that assumed for the heterogeneous catalytic and photocatalytic transformation or degradation of amines [7, 8].

On the basis of our kinetic, intermediate and end product investigations (Mogyoródy, submitted), we will now try to describe some of the details of the electrochemical degradation of thiocarbamates in aqueous NaCl solutions, with special attention paid to the characteristic reaction steps that occur during the degradation of the molecule part containing the N atom.

2. Experimental details

2.1. *Electrochemical conditions*

Electrochemical experiments were performed in three electrode cells, each of different construction and size, and operated in batch or continuous regimes. Generally, 100 ml undivided, thermostated, stirred glass cells with static, concentric cylinder platinum mesh working and counter electrodes and an Ag/AgCl reference electrode were used. However, occasionally DSA® (Ti–RuO_2) anode, stainless steel mesh cathode and 250 ml "flotation electrolysis" equipment were also used (Figure 1a). The flotation equipment [9] was modified (Figure 1a) so that after being introduced or recirculated, the reaction mixture would flow partly or completely through both electrodes and thus chlorous oxidation would take place in both alkaline and acidic media. Residence time was adjusted through supply and recirculation, while the rate of acidic and alkaline oxidation and pH-shift were regulated through cathode–anode distance. The latter affected both current and cell voltage. In some cases, N_2 gas was fed in. DC power was supplied by a potentiostat Electroflex EF 427 (Szeged), TL 9158 and TR-9252/A (FOKGYEM). Electrode potentials generally were 0.9–3.2 V and 3.5–8.1 V and electrolysis current $I=$ 0.1–2.8 A and 2.9–3.84 A. Anode–cathode distance was 0.3–3.5 cm. Initial NaCl concentration: 0.5–7.5 M. Temp.: 23–35 °C. Initial thiocarbamate concentration: 100–500 ppm. Total residence (retention) time: 15–60 min. Sample collection from the electrolyser occured at different electrolysis times: either during or after stopping the electrolysis, 5 ml solvent was poured into the cell, then mixed, shaken and separated.

In the electrochemical degradation of wastewater containing several hundred ppm thiocarbamate a supplementary UV photolysis treatment was also used. In most cases UV light was produced with commercial 125–350 W medium pressure Hg lamps. The reactor was a double wall tube made of quartz and Pyrex glass (Figure 1b).

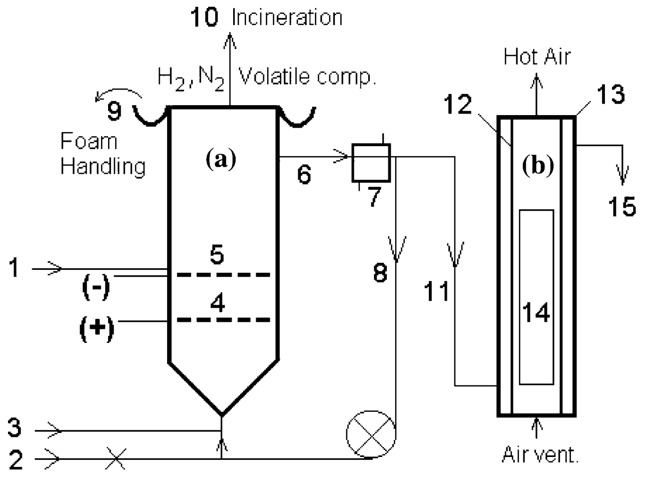
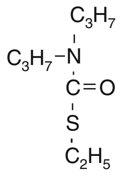


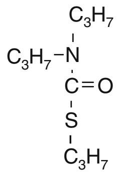
Fig. 1. Flotation electrolysis or electrolysis reactor with possible flotation (a) and UV photolysis (b) equipment for treatment of wastewaters containing thiocarbamate pesticides (or organics) and NaCl. (1)–(2) Input of wastewater and of gases and inerts (3); (4) Anode DSA® (Ti–RuO_2, IrO_2); (5) Cathode (Fe); (6) Output; (7) Water Cooler; (8) Recycling; (9) Foam Handling; (10) Incineration; (11) Input of UV Photoreactor; (12) Quartz Tube; (13) Pyrex Glass Tube; (14) 175 W Hg lamp; (15) Output of Photoreactor.

2.2. *Materials*

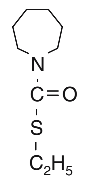
Analytical grade reagents were used and the purity of the thiocarbamate active ingredients EPTC, Vernolate and Molinate was 99.8 w/w% in all cases. All these thiocarbamates were produced by North-Hungarian Chemical Works.



EPTC



Vernolate



Molinate

2.3. *Analysis*

Thiocarbamates and their electrochemical degradation intermediates were identified and measured by High Performance Liquid Chromatograph (HPLC) or Gas Chromatograph (GC) and Gas Chromatograph/Mass Spectrometer (GC/MS) methods [10]. In HPLC measurements HP 1084D and Shimadzu chromatographs were applied. In GC analyses a given amount of solvent (CCl_4, hexane) was added to the reaction mixture. After mixing, shaking and pH adjustment, the extract was separated and 0.2 μl was fed into the Chrompack CP 9000 gas chromatograph; Column: 3 m × 2 mm metal.

GC/MS analysis was conducted using an HP 5710A coupled with a VG-7035 mass spectrometer equipped with a combined electron impact/chemical ionisation source commonly used for analysis [10]. Standards were synthetised in different ways (Mogyoródy et al., unpublished work). Total Organic Carbon (TOC) content was measured by Heraeus Liqui TOC or by Analysesystem GmbH Elementar High TOC equipment. The former is a UV – persulphate – phosphoric acid method; the latter involves the use of a high temperature furnace.

Chemical Oxygen Demand (COD) measurements were carried out with potassium bichromate. High NaCl concentrations caused a problem with both COD and TOC analyses; this was solved by adding $HgSO_4$. Cl^- concentration was specified by potentiometric titration with $AgNO_3$. SO_4^{2-} concentration was measured by gravimetric or photometric $BaCl_2$ methods, while NO_3^- concentration was determined by the photometric Na-salicylate method.

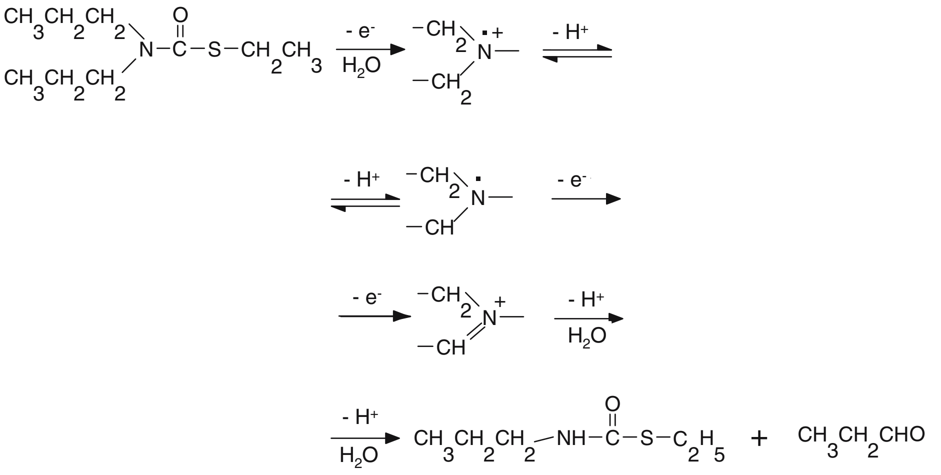
3. Results and discussion

Redox equilibria may arise in aqueous NaCl electrolyte solution, with the involvement of inorganic intermediates (Cl_2, ClOH, ClO^-, Cl_2O, H^+, OH^-, $OH^{\cdot}$,...) generated from NaCl by electrolysis. Such equilibria have already been observed and examined during water chlorination, and in Cl_2–H_2O and Cl_2–H_2O–NaCl systems [11, 12]. Electrochemical oxidation of thiocarbamates and their degradation intermediates were studied in different domains [Cl_2 (pH = 1; Pot.: 1.45 V), HClO (pH = 4; Pot.: 1.6 V), Cl^- (pH = 7; Pot.: 1.1 V), ClO^- (pH = 11; Pot.: 1.3 V)] of Cl_2–H_2O–NaCl equilibrium in 0.5 M NaCl solution. Initial EPTC concentration: 100 ppm; Pt–Pt electrodes; Temp.: 35 °C.

During the investigations either different intermediates were produced under different reaction conditions or the ratio of concentrations differed. Table 1 shows the distribution of the intermediates produced in electrochemical oxidation in Cl_2, ClOH, ClO^- and Cl^- domains of Cl_2–H_2O–NaCl equilibrium according to their gas chromatographic retention times (T_R).

Of the intermediates, $T_R = 1.63$ diethyl-disulphide is produced in all four domains, while $T_R = 2.16$, 2.3 and 3.63 intermediates come into being in Cl_2 (pH = 1) and ClOH (pH = 4) domains, and $T_R = 2.56$ EPTC-sulphoxide and $T_R = 2.83$ EPTC-sulphone are produced in the pH = 7 or in the pH = 11 ranges. Table 2 shows a typical group of degradation intermediates detected in EPTC electrochemical degradation.

This intermediate group mainly consists of amines and amine derivatives (Table 2. No. 4–9), which are produced by chlorination or chlorine substitution during the degradation of the part of the molecule containing the N atom or in the reaction of intermediates (No. 8).



(2)

Of amine intermediates, secondary amines – especially di-*n*-propylamine – occur most frequently in EPTC electrochemical degradation, but hexamethylene-imine is also produced during Vernolate and especially Molinate degradation.

In further degradation of alkyl chains of amines, chlorinated methane and ethane derivatives (No. 1–2) occur, and, as a result of oxidation, aldehydes and carboxylic acids also appear (No. 3). In addition, oxidation may take place both without (No. 10–11) and with partial (No. 12–14) degradation. Intermediates No. 12–14 were also detected and identified earlier in EPTC TiO_2 photocatalytic degradation [10]. This means they are not only produced in anodic oxidation but also under other oxidation conditions.

On the basis of the aforesaid and our experimental results, it is assumed that in electrochemical oxidation of thiocarbamates (Pt–Pt electrodes, Pot.: 1.4–1.6 V) one of the degradation routes is dealkylisation

$$\underset{\text{EPTC}}{(CH_3CH_2CH_2)_2N{-}CO{-}S{-}CH_2CH_3} \longrightarrow \underset{N\text{-depropyl-EPTC}}{CH_3CH_2CH_2NH{-}CO{-}S{-}CH_2CH_3} \qquad (1)$$

where e.g. depropylised EPTC is produced from EPTC. This was verified with both GC and GC/MS analysis. *N*-depropyl-EPTC standard was produced in the synthesis of *n*-propyl-amine and ethyl-chloro-thioformiate (ECTF) and was also identified this way.

Dealkylisation takes place relatively easily so that the formation of *N*-depropyl-EPTC is also detected in both EPTC aqueous chlorination and in hydrolysis in aqueous medium. Thus it is not specifically a product of electrolysis since the oxidising materials (HClO, ClO^-, Cl_2O,...) present in the Cl_2–H_2O equilibrium system, and often even atmospheric oxygen, may trigger the reaction

The other product is propyl-aldehyde. The mechanism suggested is similar to the mechanism hypothesised by

Table 1. Occurrence (+) and non-occurrence (–) of EPTC electrolysis intermediates in different domains in Cl_2–H_2O–(NaCl) equilibrium systems according to gas chromatographic retention times (T_R). EPTC initial conc.: 100 ppm; $[NaCl]_0 = 0.5$ M l^{-1}; Pt–Pt electrodes, Temp.: 35 °C

T_R	Cl_2, pH = 1, Pot.: 1.45 V	HOCl, pH = 4, Pot.: 1.6 V	OCl^-, pH = 11, Pot.: 1.3 V	Cl^-, pH = 7, Pot.: 1.1 V
1.63	+	+	+	+
2.3	+	+	+	–
2.16	+	+	–	–
3.63	+	+	–	–
2.56	–	–	+	+
2.83	–	+	+	+
3.88	–	+	–	–

Table 2. Intermediates detected in EPTC electrochemical degradation. Degradation intermediates of molecule section containing N atom

1. $CHCl_3$, CH_2Cl_2	Chlorinated methane derivatives
2. $CHCl_2CH_3$, CH_2ClCH_2Cl	Chlorinated ethane derivatives
3. C_2H_5CHO, CH_3CHO, CH_3COOH	Aldehydes, carboxylic acids
4. $(C_3H_7)_2NH$, $(C_3H_7)_2NC_2H_5$	Di-*n*-propyl-amine, ethyl-di-propyl-amine
5. $(C_3H_7)_2NCl$	Di-*n*-propyl-chloramine
6. NCl_3, $NHCl_2$, NH_2Cl	Chloramines
7. $(C_3H_7)_2NCOCl$	Di-*n*-propyl-carbamoil-chloride
8. $(C_3H_7)_2NCON(C_3H_7)_2$	Tetra-propyl-carbamide
9. $C_3H_7NHCOSC_2H_5$	*N*-depropyl-EPTC
10. $(C_3H_7)_2NCOSOC_2H_5$	EPTC-sulphoxide
11. $(C_3H_7)_2NCOSO_2C_2H_5$	EPTC-sulphone
12. $(C_3H_7)CHONCOSC_2H_5$*	
13. $(C_3H_7)(CH_3COCH_2)NCOSC_2H_5$*	
14. $(C_3H_7)CHOC_2H_4NCOSC_2H_5$*	

*Detected intermediates.

Wei and Stewart for alkali permanganate oxidation of primary amines [6], and to our photocatalytic thiocarbamate degradation mechanism [10]. Dealkyl-EPTC intermediate formation is notable because it largely determines further EPTC degradation. It was observed that if dealkyl-EPTC appears, degradation through a sulphoxide intermediate decreases. In most cases, sulphoxide formation cannot even be detected and no sulphoxide is formed from dealkyl-thiocarbamates (*N*-monoalkyl-thiocarbamates). With the help of T. Patonai and B. Lévai, this was experimentally verified (Mogyoródy et al., unpublished work) and thus confirms the negative results obtained by Barton et al. concerning *m*-Cl-perbenzoic acid oxidation [13]. Dimethyl-dioxirane oxidation gave the same result (Mogyoródy et al., unpublished work). Thus it is no coincidence that during electrolysis *N*-depropyl-EPTC was detected as an intermediate in the Cl_2 and HOCl domains, while EPTC-sulphoxide was not.

During degradation, *N*-depropyl-EPTC may be further depropylised in a mechanism similar to the previous one

$$\begin{aligned}&CH_3CH_2CH_2{-}NH{-}CO{-}S{-}C_2H_5\\&\quad\rightarrow H_2N{-}CO{-}S{-}C_2H_5 + CH_3CH_2CHO\end{aligned}\tag{3}$$

Here NH_3 is produced by thioamide degradation probably through the H_2N–CHO intermediate. Ammonium may react immediately in aqueous-acidic, chlorine or hypochlorous acid solutions [14–16] so we may suppose that according to the formulae

$$\begin{aligned}&NH_3 + HOCl \rightarrow NH_2Cl + H^+(+OH^-)\\&NH_2Cl + HOCl \rightarrow NHCl_2 + H^+(+OH^-)\\&NHCl_2 + HOCl \rightarrow NCl_3 + H_2O\end{aligned}\tag{4}$$

chloramines are also formed during electrochemical thiocarbamate degradation in NaCl solutions. They were identified by both GC measurements and preparative experiments. Figure 2 shows the GC chromatogram of the CCl_4 extract of the electrolysis reaction mixture containing NH_2Cl, $NHCl_2$ and NCl_3 ($T_R = 6.31$).

At the same time, NH_3 may react with oxidising species that play a role in electrochemical oxidation. As a result, NO_3^- may be produced through NO_2^- in a process not yet fully understood, according to [17]:

$$NH_3 \xrightarrow[H_2O]{} (\text{intermediate}) \xrightarrow[H_2O]{OH} NO_2^- \xrightarrow{HO_2^-} NO_3^- \tag{5}$$

In any case, it is important to consider whether degradation takes place in a chloro amine or a nitrate pathway. If both options have to be taken into account it has to be specified what their ratio is. The latter also depends on the pH.

Chloramines are produced faster in acidic, Cl_2 ($pH < 4$) or HOCl ($pH = 4–7$) medium than in alkaline ($pH > 7$) medium [18]. Because of this, a greater part of the degradation process probably takes place through chloramines, although their degradation is quicker in alkaline medium [19] because in acidic pH.

$$\begin{aligned}&2NH_2Cl + H^+ \rightleftharpoons NHCl_2 + NH_4^+\\&3NHCl_2 + H^+ \rightleftharpoons 2NCl_3 + NH_4^+\\&NH_2Cl + NHCl_2 + H^+ \rightleftharpoons NCl_3 + NH_4^+\end{aligned}\tag{6}$$

degradation may slow down due to the disproportionation equilibria (especially the first). At the end of the process, ammonium remains and may then be transformed into NO_3^- in the above-mentioned way.

In alkaline ($pH = 8–12$) medium both chloramine hydrolysis and degradation are quicker [18, 19]. During the reactions N_2 gas (which, unlike NO_3^-, is

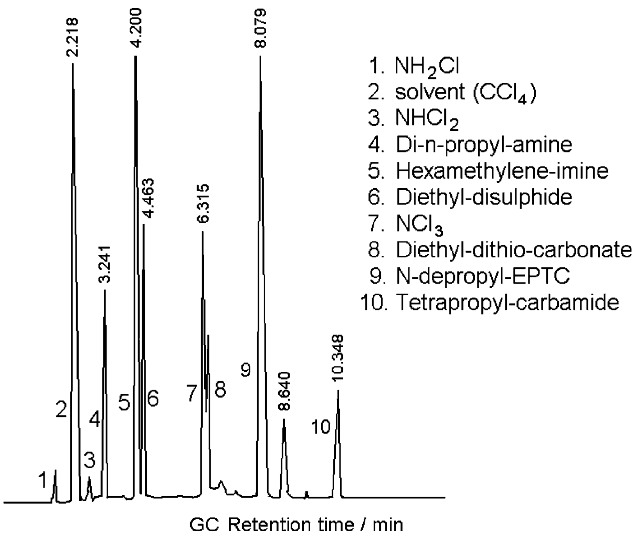


Fig. 2. GC chromatogram of CCl_4 extract of reaction mixture containing dealkyl-EPTC ($T_R = 8.079$), NCl_3 ($T_R = 6.315$) and other identified intermediates. Electrolysis conditions: one chamber cell with Pt–Pt electrodes; Pot.: 1.5 V; pH = 4.0; Initial EPTC conc.: 192 mg l^{-1}; $[NaCl]_0 = 150$ g l^{-1}; $t = 45$ min.; Temp.: 30 °C.

non-polluting) is also formed, depending on the pH and reaction conditions (e.g. Cl^- concentration):

$$\begin{aligned} &2NHCl_2 + 4OH^- \longrightarrow N_2 + 3Cl^- + OCl^- + 3H_2O \\ &NHCl_2 + NCl_3 + 3OH^- \longrightarrow N_2 + 2HOCl + 3Cl^- + H_2O \end{aligned} \tag{7}$$

In the OCl^- domain, at around $pH = 10–11$, NCl_3 degradation is complete [18]. The $NHCl_2$ and NCl_3 mixture already degrades quickly in less alkaline ($pH = 8–9$) or neutral ($pH \approx 7$) medium by an autocatalytic mechanism.

$$\begin{aligned} &NHCl_2 + HOCl \longrightarrow NCl_3 + H^+ + OH^- \\ &NHCl_2 + NCl_3 + 3OH^- \longrightarrow N_2 + 2HOCl + 3Cl^- + H_2O \end{aligned} \tag{8}$$

Increasing Cl^- concentration can further accelerate this process [18]. In this way the chloride ion indirectly accelerates NCl_3 degradation and in the long run also the degradation of the N containing part of the thiocarbamate molecule into N_2 (not only into NO_3^-).

On the basis of the aforementioned, in the ranges of 1.1–1.9 V (Pt–Pt) and 3.2–8.1 V (DSA-Fe) electrode potentials, we propose the following mechanism scheme for the electrochemical degradation of the N containing part of the thiocarbamate molecule in NaCl solutions (Figure 3).

Degradation may start with the breaking up of the N–C and C–S bonds. After this the intermediates are transformed into NH_3 or NCl_3 intermediates through oxidation (a) or chlorination (b) pathways. Then, depending on reaction parameters, primarily on pH, degradation continues in the direction of NO_3^- (a) $pH < 7$ or N_2 (b) $pH > 7$ end product, or in both directions.

That the mechanism described above is valid is demonstrated by the fact that the NO_3^- concentration was significantly higher in electrolysis performed in acidic medium ($pH = 6$), than in alkaline ($pH = 12$) under otherwise identical reaction conditions (Table 3). This tendency was typical for the classes of synthetic systems chosen for investigation.

Table 3 shows that a greater amount of NO_3^- is produced during "acidic" ($pH < 6$) electrolysis, while a greater amount of SO_4^{2-} is produced during "alkaline" ($pH > 8$) electrolysis. Therefore, if the goal is to produce the greatest amount of sulphate and N_2 gas and the smallest amount of nitrate during electrolysis, then the process should be started in alkaline medium to promote sulphoxide intermediate formation and at the same time to restrict nitrate production (Table 3). On the other

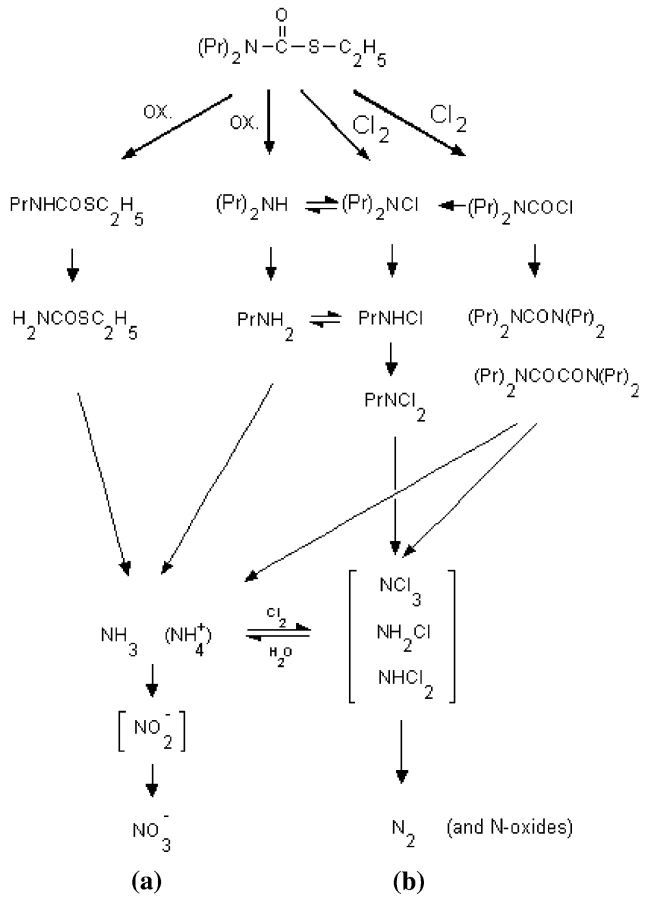


Fig. 3. Degradation of thiocarbamate molecule parts containing N atom. Some typical degradation mechanism pathways in thiocarbamate (EPTC) electrochemical degradation in Cl_2, HOCl, OCl^- and Cl^- domains of NaCl solutions.

Table 3. Electrolysis of Molinate industrial wastewater [2]. Pt–Pt electrodes, Pot. = 1.7 V, $pH_1 = 6$, $pH_2 = 12$, $t = 60$ min., $[Cl^-]_0 = 173.95$ g l^{-1}

	NO_3^-/mg l^{-1}	SO_4^{2-}/mg l^{-1}
Start	6.6	49.3
"Acidic" electrolysis	22.0	385.2
"Alkaline" electrolysis	11.75	439.5

hand, in order to get sulphoxide (for example EPTC-sulphoxide, $T_R = 2.56$) to degrade quickly, electrolysis should be continued in neutral or slightly acidic medium. The latter, in turn, promotes NCl_3 formation, so its degradation is best achieved by realkalising the medium. Alkaline medium restricts NO_3^- formation (Table 3) and promotes N_2 gas production (Figure 3), which is non-polluting and increases electrolysis safety. Safety can be additionally enhanced by feeding in additional N_2 or inerts, which help in the regulation of gas bubble rising velocity and foam handling.

Electrolysis involving pH-shift and recirculation can be performed through the modification of the flotation method called electroflotation [9] as well as through the introduction of an electrolysis method with flotation, because the added and/or released gases may produce foam (Figure 1).

The acid (HCl) formed during the hydrolysis of Cl_2 produced on the anode and the base (NaOH) produced on the cathode is enough in continuous flow-through operational mode to achieve pH-shift without the addition of further reagents. By varying the distance between electrodes and recirculation rate, both pH and residence time can be regulated. If it is performed in this way, "flotation electrolysis" is enough in itself to decontaminate wastewater containing 100–200 ppm organic material on average (in this case EPTC herbicide active ingredients) (Figure 4).

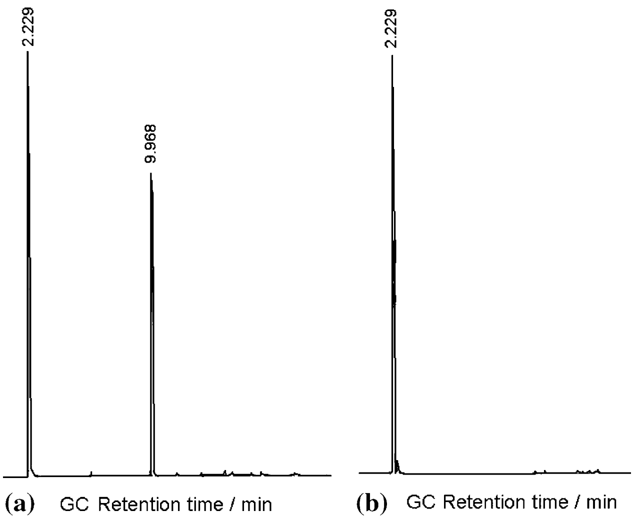
Figure 4 shows that after flotation electrolysis, the EPTC peak (Figure 4a), which can be seen in the GC chromatogram of the CCl_4 extract of a concentrated (27 w/w%) NaCl solution originally containing 192 ppm EPTC, does not even appear (Figure 4b). Consequently, after flotation electrolysis, EPTC or organic material contamination cannot even be detected with GC method, where the lower measurement limit is below 1 ppm.

If wastewater contains a higher amount of organic material with N atoms, e.g. if it contains 500 ppm Molinate, then, depending on the parameters, more chloramine, e.g. NCl_3, is produced during electrolysis. This decreases process safety because, besides temperature, one of the most decisive sensitivity properties of NCl_3 is its concentration in the solution. NCl_3, however, is sensitive to UV light [20, 21]. Our investigations demonstrate that under the applied reaction conditions NCl_3 can also be degraded by UV photolysis (Figure 5a–c).

By using electrochemical treatment (flotation electrolysis), initial Molinate contamination (a) disappears, and the NCl_3 intermediate (b) formed is degraded by UV irradiation (c). According to the gas chromatogram (C), the treated NaCl solution contains neither organic pollutants nor chloramines and can be safely electrolysed and the NaOH solution produced can be recirculated as acid-acceptor to thiocarbamate synthesis.

4. Conclusion

In NaCl solutions electrochemical oxidation using an undivided cell (Pt–Pt, Ag/AgCl), Pot.: 1.1–1.7 V) or a flotation electrolysis cell (DSA-Fe, Pot.: 3.2–8.1 V), can be applied in the degradation of organic thiocarbamate pollutants containing N atoms. We have confirmed this with the identification and investigation of intermediates.



(a) GC Retention time / min **(b)** GC Retention time / min

Fig. 4. EPTC electrochemical degradation in cc. NaCl solution. (a) GC chromatogram before electrochemical treatment. (EPTC $T_R = 9.968$ min); (b) GC chromatogram after electrochemical treatment. (No EPTC detected). Electrochemical conditions: Flotation Electrolysis (Figure 1); Initial EPTC conc.: 192 ppm; $[NaCl]_0 = 27$ w/w%; Temp.: 35 °C; Tot. Ret. Time in Reactor: 45 min.

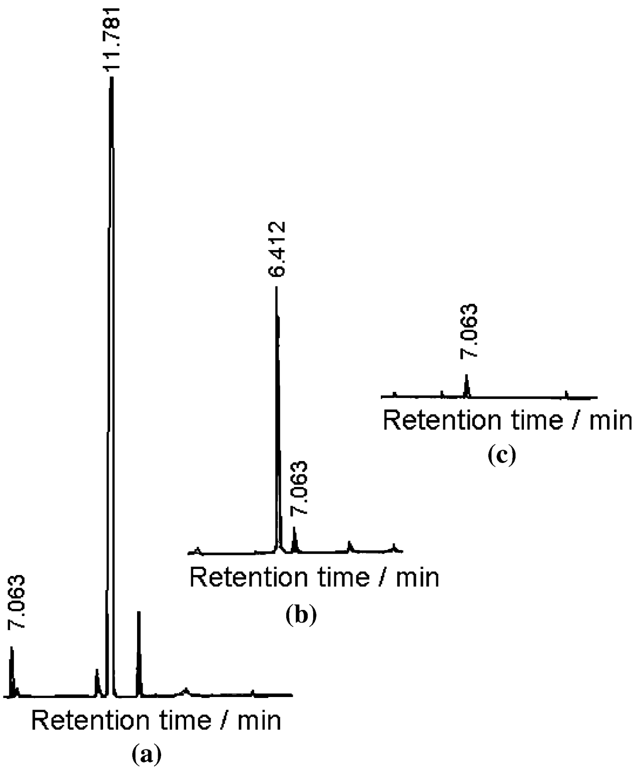


Fig. 5. Electrochemical and UV photochemical (Figure 1) degradation of thiocarbamate Molinate. (a) GC chromatogram of initial Molinate solution. (Molinate $T_R = 11.781$ min); (b) GC chromatogram after electrochemical treatment. (NCl_3 $T_R = 6.412$ min); (c) GC chromatogram after UV treatment (125 W Mercury lamp). (No Molinate and NCl_3 detected). Electrochemical conditions: $[\text{Molinate}]_0 = 500$ ppm; $[NaCl]_0 = 27$ w/w%; DSA-Fe electrodes; Pot.: 8.11 V; $I = 3.84$ A; $pH_1 = 6$; $pH_2 = 12$; Temp.: 35 °C; Tot. Ret. Time: 60 min.

It has been concluded that, depending on the reaction parameters used ($[NaCl]_0 = 0.5$–7 M l^{-1}, Pot.: 1.1–1.7 V, pH = 1–12) in electrolysis, Cl_2–H_2O equilibria affect intermediate formation and degradation and end product formation. In the 1–7 pH range more chlorinated intermediates are produced, while at neutral and alkaline pH values (pH = 7–12) more oxidation intermediates are formed. Intermediates may react with one another, which leads to the formation of further intermediates that, in turn, modify the degradation process.

The identification of intermediates helped us to define reactions, reaction pathways and a simplified schema of the degradation process mechanism. On the basis of this mechanism we can now explain both the electrolysis reaction process performed in acidic and alkaline reaction media, and intermediate and end product formation. Additionally, the scheme demonstrates that sulphate formation occurs preferably in alkaline reaction medium, while nitrate formation tends to occur preferably in acidic reaction medium. The mechanism scheme and the reactions also reveal that nitrate end product formation can be restricted and N_2 gas formation can be promoted through the selection and proper adjustment of reaction parameters, primarily pH. To implement this, a modified version of the electroflotation method called "flotation electrolysis" has been found to be most effective as it facilitates a regulated pH shift, foam handling and gas bubble rising velocity. Especially when supplemented with UV photolysis, it has proved to be a reliable, safe method for the electrochemical treatment and decontamination of wastewater containing NaCl and thiocarbamate pesticides.

Acknowledgements

The author is grateful to Prof Lajos Papp and Prof George Kaptay for their support.

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