

Influence of chlorine-water equilibria on the electrochemical destruction of thiocarbamate herbicides in NaCl solutions

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Abstract

The electrolytic destruction of thiocarbamates in NaCl solutions takes place mainly through indirect electrolysis with Cl_2 , HOCl , ClO^- and other oxidising species. The electrochemical destruction of thiocarbamates EPTC and Vernolate was studied in different Cl_2 , HOCl , ClO^- domains in chlorine–water equilibrium. Differences were found in both destruction rate and in intermediate and end products. Complete mineralisation can be achieved in ClO^- domain, where both total organic carbon (TOC) content and chemical oxygen demand (COD) are continuously decreasing and biodegradability is increasing during electrolysis. UV irradiation considerably accelerates the destruction process, i.e. the electrochemical destruction of thiocarbamate Vernolate.

1. Introduction

Thiocarbamate herbicides and insecticides are used worldwide in agriculture because they can be used selectively in pest control and degrade in soil relatively easily [1–3].

Due to partial water solubility [4, 5], thiocarbamate herbicides and insecticides may appear as pollutants in groundwater, surface water and in drinking water alike [6]. Owing to their volatility they may even get into the upper atmosphere [7].

Thiocarbamate aqueous solutions (5–10 ppm) may be completely decontaminated by photocatalytic method [8]. Our preliminary investigations also revealed that higher concentrations (100–200 ppm or above) made it difficult to use a photocatalytic method. In the decontamination of more concentrated NaCl-solutions, e.g. technological wastewater, TiO_2 photocatalysis cannot be applied.

For decontamination of wastewaters with 8–20 % (w/w) NaCl-content, not even advanced oxidation processes (AOPs) offer economical solutions due to the high Cl^- -ion content. Cl^- -ions affect the process adversely as they consume a considerable amount of oxidizing agents. For the removal of thiocarbamates from such wastewaters, the electrochemical method was found to be the most efficient (F. Mogyoródy, 2005, submitted).

The mediating role of chloride ion and the effect of chloride concentration on anodic mineralisation of organic substrates in chloride-containing aqueous media

in the electrochemical incineration of glucose have already been discussed [9]. The influence of Cl^- -ion depends not only on the oxidation process but also on the type of electrode used [10–12].

Direct and indirect electrochemical methods offer promising solutions to pollution prevention and remediation. Indirect electrolysis uses electrochemically generated redox reagents such as chlorine, hypochloric acid, hypochlorite, OH^- and peroxide. All these can also be produced in the electrolysis of organic wastewater solutions with NaCl content. In the treatment of thiocarbamate industrial wastewater with high NaCl content, indirect electrolysis can be used as a chemical on/off switch process which requires no extra reagents (F. Mogyoródy, 2005, submitted).

The process starts on the electrode with oxidising NaCl electrolysis intermediate formation. It continues and ends with the decomposition of the thiocarbamate ‘mother compound’ and its degradation intermediates. In water solution NaCl electrolysis intermediates take part in several interdependent equilibria. The effect of chlorine–water equilibrium should also be taken into account. Equilibrium relations in aqueous chlorine solutions have already been examined [13–16]. The ratio of mol fractions Cl_2 , HClO and ClO^- has been thoroughly investigated as a function of pH [17].

The present work investigates under what electrolysis reaction conditions and equilibria parameters thiocarbamate and intermediate destruction occurs most efficiently.

2. Experimental details

2.1. Electrochemical conditions

Electrochemical experiments were made in three electrode cells of different construction and size (F. Mogyoródy, 2005, submitted). In general, platinum mesh working and counter electrodes, and an Ag/AgCl electrode as reference were used with DC power supply, TL 9158 and TR-9252/A (FOKGYEM), and EF 427 Potentiostat Electroflex (Szeged).

The standard working compartment of the cell had an approximate volume of 100 cm³ and was degassed with nitrogen. Controlled potential electrolysis was performed using the same cell and configuration of electrodes and electrolysis parameters. UV irradiation was conducted using a quartz tube cell, 125 W Mercury lamp and water cooler.

2.2. Materials

All reagents used were of analytical grade. The purity of thiocarbamate active ingredients EPTC $\{(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NCOSCH}_2\text{CH}_3\}$ and Vernolate $\{(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NCOSCH}_2\text{CH}_2\text{CH}_3\}$ was 99.9%(w/w), each produced by North-Hungarian Chemical Works. Pro-analysis grad NaCl (Reanal) and double-distilled water were used. Solution pH was adjusted by NaOH, 37.5%(w/w) HCl and perchloric acid. All of them were pro-analysis grade (Reanal).

2.3. Analysis

During electrolysis, the electrolyte was periodically sampled and analysed by HPLC or GC. Solution UV absorbance was continuously measured by diode array spectrophotometer (F. Mogyoródy, 2005, submitted).

Degradation intermediates were identified with retention time (R_t) in HPLC or in GC analysis. By the help of Z. Dinya analysis was also performed with HP 5710A coupled with VG-7035 mass spectrometer equipped with a combined electron impact/chemical ionisation source [6, 8]. All the intermediates (Figure 2) were then identified by qualitative analysis at least. EPTC-sulphoxide, Vernolate-sulphoxide and other standards (Figure 2) were synthesised in different ways [18–20]. (see later)

Total organic carbon (TOC) content of initial and electrolysed solutions was determined on Heraeus Liqui TOC 2001 analyser by low temperature UV-peroxodisulphate oxidation method and on an Analysystem GmbH Elementar High TOC analyser employing catalytic high temperature furnace oxidation.

Chemical oxygen demand (COD) was specified by standard potassium-dichromate method with HgSO₄ additive.

UV photolysis treatment was performed in a quartz tube cell. UV light was produced with commercial medium pressure mercury lamps (125–350 W).

Biodegradability of thiocarbamate active ingredients and their destruction intermediates was studied with biological oxidation method using active sludge with living bacterial strains. The method is called rapid biological oxygen demand (RBOD). It is based on the measurement of oxygen concentration in active sludge mixed continuously by bubbling oxygen. When the sample containing organic waste is injected into the sludge, the biodegradable organic material consumes the oxygen and the change of oxygen concentration is proportionate to degraded organic compound concentration. Na-acetate was used as a standard. Biodegradability was calculated as RBOD/COD in %.

Sulphate was analysed by gravimetric and/or by photometric (ASTM, p. 593–594) and nitrate by photometric Na-salicylate method. Initial free available chlorine was determined either iodometrically or by UV spectrophotometric (Cl₂: 330 nm; HClO: 236 nm; ClO⁻: 292 nm) way.

3. Results and discussion

It was found that thiocarbamate electrolytic destruction takes place mainly in the parts either near to or far from the electrode in aqueous NaCl solutions (F. Mogyoródy, 2005, submitted). Therefore it is not surprising that the duration of the destruction process is very similar in both electrochemical (Figure 1a) and hypochlorous destruction (Figure 1b) for the herbicide Vernolate, even though the starting conditions (Vernolate concentration, NaCl concentration, pH) were not completely identical.

Vernolate concentration decreased rapidly while an essential intermediate was produced, which was the same in both cases. Its concentration varied according to a maximum curve with a similar type of decay (an intermediate which is rapidly produced and then slowly degrades). This intermediate was Vernolate-sulphoxide $\{(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NCOSCH}_2\text{CH}_2\text{CH}_3\}$ identified by both HPLC and GC/MS and on the basis of standard samples.

The standard samples were prepared from EPTC and Vernolate active ingredients with both the method involving per-formic acid (H₂O₂ + HCOOH) and the one involving oxidation with m-Cl-perbenzoic acid [19–21] and a reaction with dimethyl-dioxirane. Then they were checked by thin-layer chromatography.

The electrochemical chlorous oxidation of Vernolate and chlorous oxidation in a homogeneous liquid phase were similar if other reaction parameters were identical. Probably this was because a similar redox equilibrium occurred in the solution, with inorganic intermediates (Cl₂, HClO, ClO⁻, Cl₂O, H⁺, OH⁻, OH[•],...) generated from NaCl by electrolysis. Such equilibria have already been observed and examined during water chlorination and in Cl₂-H₂O and Cl₂-H₂O-NaCl systems [13–17].

It is known that the predominant chlorine species present in the pH range 1–3 is chlorine. HClO

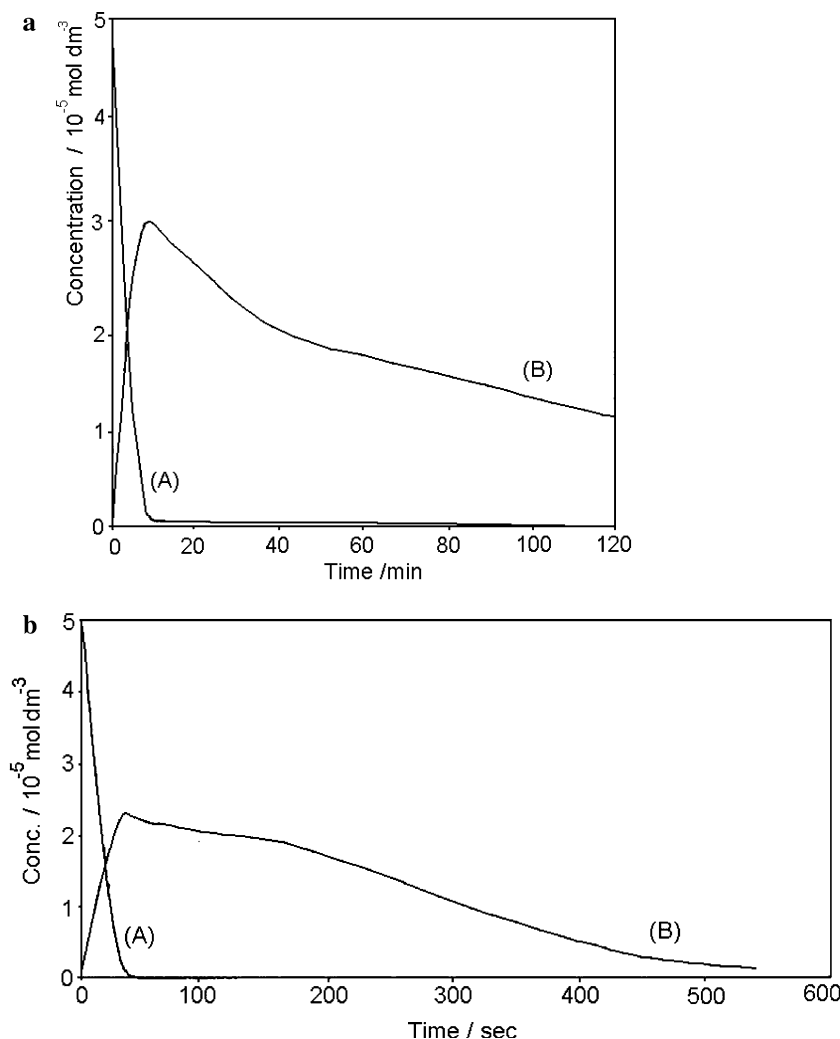
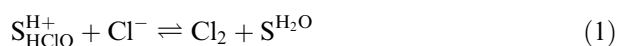


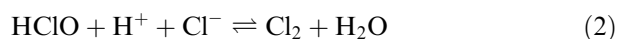
Fig. 1. (a) Electrochemical destruction of Vernolate in 0.5 mol dm^{-3} NaCl solution. Change of concentration of (HPLC $R_t=20.98$) Vernolate (A) and of intermediate ($R_t=3.18$) Vernolate-sulphoxide (B) in time. Initial conc. of Vernolate: $4.7 \times 10^{-5} \text{ mol dm}^{-3}$; pH = 6.5; Pt-Pt electrodes; Pot.: 1.42 V; Temp.: 35°C . (b) Hypochlorous destruction of Vernolate. Change of concentration of Vernolate (A) $R_t=20.98$ and of intermediate Vernolate-sulphoxide (B) $R_t=3.18$ in time. Initial conc. of Vernolate: $4.7 \times 10^{-5} \text{ mol dm}^{-3}$; Conc. of free avail. Cl_2 : $2.2 \times 10^{-4} \text{ mol dm}^{-3}$; pH = 7; Temp.: 35°C .

predominates in the pH range 5–7 and ClO^- is the major species present above pH 8 [16]. The ratio between mol fractions Cl_2 , HClO and ClO^- as a function of pH has also been thoroughly investigated [17].

On the basis of the previously discussed preliminary studies (F. Mogyoródy, 2005, submitted), during NaCl electrolysis in Cl_2 domain ($\text{pH}_0=1$, $[\text{NaCl}]_0=5 \text{ mol dm}^{-3}$), predominantly Cl_2 is formed from HClO in reaction



on the anode surface [18] and/or after desorption in the solution in



equilibrium reaction. This is indicated by the fact that during NaCl electrolysis in the solution, the concentration of less reactive HClO increases faster than Cl_2 concentration, and UV absorptivity (A) or absorbance

ratio of $A_{\text{Cl}_2}/A_{\text{HClO}}$ is only 0.1–0.3 (F. Mogyoródy, 2005, submitted).

The use of higher Cl^- and H^+ concentrations may shift the equilibria (2) towards forming more Cl_2 . This way, chlorination may occur to a greater extent and more chlorinated organic intermediates and products may be produced in electrophyl substitution reaction



Because of the relatively high $A_{\text{HClO}}/A_{\text{Cl}_2}$ ratio (F. Mogyoródy, 2005, submitted) or HClO concentration, $\text{Cl}_2\text{O} \cdot \text{H}_2\text{O}$ is formed from HClO [22] in equilibrium reaction.



As Cl_2O is much more reactive than HClO , it should be considered a potential reactant. The role of HClO (or Cl_2O) as predominant reagent is more marked in the less acidic (pH 3.5–6.5) HClO domain. At the same time, the

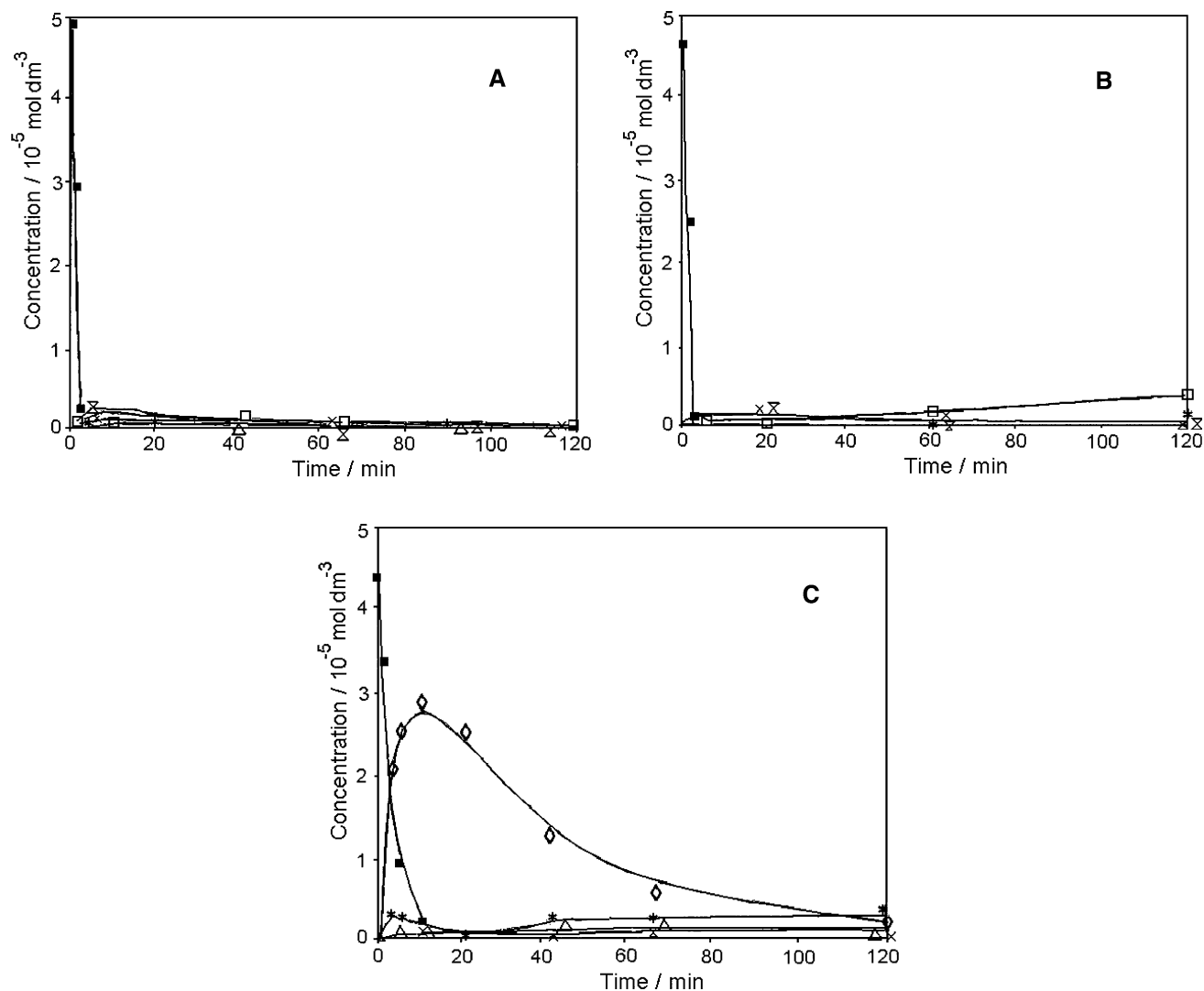


Fig. 2. (A–C) Electrochemical decomposition of EPTC ■ and its degradation intermediates in different (A: Cl_2 ; B: HOCl ; C: ClO^-) domains of Cl_2 - H_2O equilibrium in 0.5 M NaCl solution. Initial conc. of EPTC: $5.3 \times 10^{-5} \text{ mol dm}^{-3}$; Pt–Pt electrodes; Temperature: 35 °C. A(Cl_2): pH = 1; Pot.: 1.45 V; B(HOCl): pH = 4; Pot.: 1.6 V; C(ClO_2^-): pH = 11; Pot.: 1.3 V; R_t = GC Retention Time (min.) of degradation intermediates: ■ $R_t = 1.63$ [$\text{C}_2\text{H}_5\text{SSC}_2\text{H}_5$, diethyl-disulphide]; □ $R_t = 2.16$ [$(\text{C}_3\text{H}_7)_2\text{COCl}$, di-propyl-carbamoil-chloride]; × $R_t = 2.3$ [$(\text{C}_2\text{H}_5\text{S})_2\text{CO}$, di-ethyl-dithiocarbonate]; ◆ $R_t = 2.56$ [$(\text{C}_3\text{H}_7)_2\text{NCOS(O)C}_2\text{H}_5$, EPTC-sulphoxide]; ▲ $R_t = 2.83$ [$(\text{C}_3\text{H}_7)_2\text{NCOSO}_2\text{C}_2\text{H}_5$, EPTC-sulphone]; ⊗ $R_t = 3.63$ [$(\text{C}_3\text{H}_7)\text{NCOSC}_2\text{H}_5$, N-depropyl-EPTC] Qualitative analysis of the other EPTC electrochemical degradation intermediates by HPLC, GC and GC/MS methods: Cl_2 and HClO domains: CHCl_3 , CCl_4 , $\text{C}_2\text{H}_4\text{Cl}_2$, CCl_3CHO , CH_2ClCOOH , $\text{CH}_3\text{CH}_2\text{SCL}$, $\text{CH}_3\text{CHClSCL}$, $\text{CH}_2\text{ClCHClSCL}$, $\text{C}_2\text{H}_5\text{SC}_2\text{H}_5$, $\text{C}_3\text{H}_7\text{NHCH}_2\text{Cl}$, $\text{C}_3\text{H}_7(\text{C}_3\text{H}_6\text{Cl})\text{NCOCI}$, $(\text{C}_3\text{H}_7)_2\text{NCOSCHClCH}_3$ (Chlorinated intermediates). ClO^- domain: CH_3CHO , $\text{C}_2\text{H}_5\text{CHO}$, CH_3COCH_3 , $\text{C}_3\text{H}_7\text{SSC}_3\text{H}_7$, $\text{C}_2\text{H}_5\text{SSSC}_2\text{H}_5$, $\text{C}_3\text{H}_7(\text{C}_3\text{H}_6\text{OH})\text{NCOSC}_2\text{H}_5$, $\text{C}_3\text{H}_7(\text{C}_2\text{H}_4\text{CHO})\text{NCOSC}_2\text{H}_5$, $\text{C}_3\text{H}_7(\text{CHO})\text{NCOSC}_2\text{H}_5$, $\text{C}_3\text{H}_7(\text{C}_2\text{H}_5\text{CO})\text{NCOSC}_2\text{H}_5$ (Oxidation intermediates).

role of Cl_2 decreases. In this range, ClO^- concentration increases parallel with pH increase



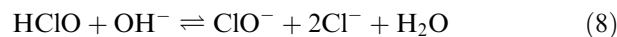
but in pH range 3–6 the ratio of $A_{\text{HClO}}/A_{\text{ClO}^-}$ is about 3–4 and changes only slightly. As ClO^- is less reactive to HClO [14–17, 22, 23], in this domain HClO (or Cl_2O) is the predominant reactant.

If H^+ -ion concentration (Eq. 5) is decreased in the neutral Cl^- domain, the $A_{\text{HClO}}/A_{\text{ClO}^-}$ ratio and $\text{Cl}_2\text{O} \cdot \text{H}_2\text{O}$ concentration also decrease because of reactions (5–7)



and because of the low equilibrium constant of Eq. (4) [23]. In 0.5 mol dm^{-3} NaCl solution with pH range close to 7 and at low potentials $E < 1.1$ V, oxygen evolution and oxidation are possible reactions.

In strong NaOH solutions above pH 9, there is basically no HClO present.



For this reason no Cl_2O can be formed according to Eq. (4). The reactivity of such an alkaline Cl_2 - H_2O -NaCl equilibrium system is lower in a ClO^- domain than in an

acidic (chlorous or hypochlorous) one. At the same time, the possibility of chlorination is smaller than that of oxidation.

In our case it was also found that aqueous chlorine solutions have chlorinating as well as oxidising properties. Depending on reaction parameters (chlorine and Cl^- contents, pH), oxidation and/or chlorination and degradation may occur simultaneously, and a chlorous (Cl_2) domain as well as domains of HClO and ClO^- can be detected.

Table 1 summarises the EPTC half-lives, pH and initial current intensity data measured in the electrolysis performed in three different domains of Cl_2 - H_2O - NaCl equilibrium system. Figure 2A-C indicates the progress of the destruction process over time.

On the basis of Table 1 and Figure 2A-C, it can be concluded that the rate and half-period of the electrochemical destruction of the EPTC "mother compound" primarily depend on current intensity and solution pH. Reaction is fastest in acidic and slightly acidic ranges, where characteristic reactants are Cl_2 and HClO , and "active" chlorine concentration is high. In alkaline (ClO^-) domain, there is a slower destruction rate.

Figure 2A-C shows that in the electrochemical destruction of EPTC, intermediates which are more stable and degrade more slowly than the EPTC mother compound are produced in different concentrations. In acidic ranges no EPTC-sulphoxide $\{(\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NCOSOCH}_2\text{CH}_2\text{CH}_3\}$ is produced, but in alkaline domains it is produced in stoichiometric proportions. Its concentration varies in alkaline (ClO^-) domain according to a maximum curve (Figure 2C), so it degrades in a further reaction. This may account for the fact that with electrolysis the complete destruction of organic material, i.e. complete mineralisation, is achieved only in ClO^- domain (Figure 3, curve (A)). Energy consumption depends highly on experimental conditions, i.e. on pH. In the reaction parameters of Figures 2C and 3, curve (A), energy consumption was 152.62 kJ g^{-1} and 62.76 kJ g^{-1} EPTC, respectively. In acidic conditions (Figure 3, curve (B) and (C)) a smaller TOC decrease could be achieved by using a higher electric charge.

Table 1. Half-lives in EPTC electrolytic degradation at the different concentration domains of Cl_2 - H_2O equilibrium in the presence of 0.5 mol dm^{-3} NaCl

| Initial reaction parameters | Domains in chlorine-water equilibrium | | |
|--|---------------------------------------|---------------|----------------|
| | Cl_2 | HOCl | OCl^- |
| pH | 1 | 4 | 11 |
| Initial current /mA | 2950 | 2050 | 620 |
| ^a Half-life $\tau_{1/2}$ /min | 1.25 | 1.15 | 5 |

EPTC initial conc.: $5.3 \times 10^{-5} \text{ mol dm}^{-3}$; Pt-Pt electrodes; single-body cell with electrolyte circulation; Temp.: 35°C .

^aonly the EPTC "mother compound".

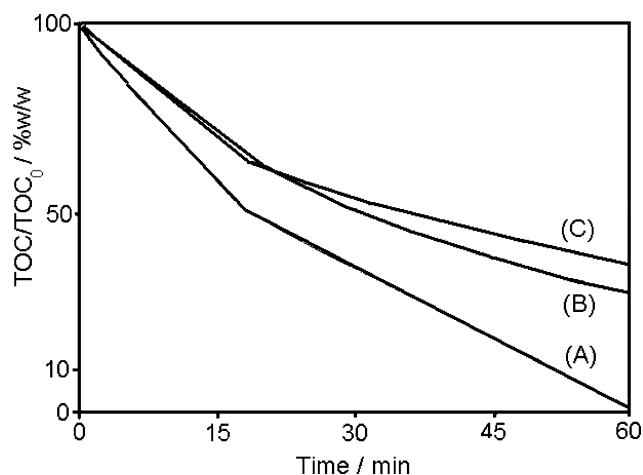


Fig. 3. Change of total organic carbon (TOC) contents in time in % (w/w) in the different domains of Cl_2 - H_2O equilibrium at the electrolytic degradation of EPTC. Initial concentration of EPTC: $5.3 \times 10^{-5} \text{ mol dm}^{-3}$; $[\text{NaCl}]_0 = 0.5 \text{ mol dm}^{-3}$; Pt-Pt electrodes; Temp.: 35°C . Domains in Cl_2 - H_2O equilibrium: ClO^- (A); Cl_2 (B); HClO (C); ClO^- (A): $\text{pH}_0 = 9.0$, Pot.: 1.3 V , $I_0 = 620 \text{ mA}$, $I_1 = 128 \text{ mA}$, measured in the interval of 5-60th min. Energy consumption of electrolytic incineration: 62.76 kJ g^{-1} EPTC.

Besides the reduction of EPTC-sulphoxide concentration, the progress of mineralisation is indicated by the resulting increase in sulphate end product concentration (Figure 4). This is also revealed in Table 2, which shows the changes in time in COD and biodegradability (BD). Table 2 shows that during electrolysis COD decreases and biodegradability increases. This indicates an increase in the biological compatibility of the treated solution.

The question arises how this reaction process, leading to complete mineralisation through a sulphoxide intermediate, could be accelerated. As we have seen, EPTC-sulphoxide is not produced in acidic domains but in alkaline medium (ClO^- domain), although its destruction is a slow process (Figure 2C). As Vernolate-sulphoxide

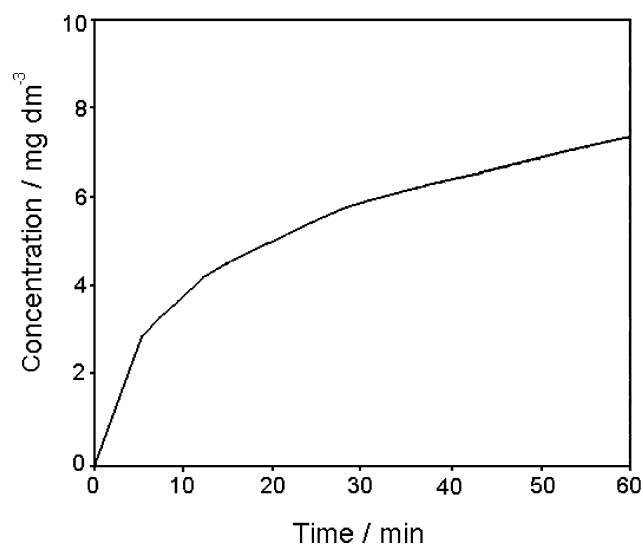


Fig. 4. Change of sulphate concentration during the electrolysis of EPTC in the area of ClO^- of Cl_2 - H_2O equilibrium. Initial EPTC concentration $5.3 \times 10^{-5} \text{ mol dm}^{-3}$; $\text{pH} = 11$; Pot.: 1.3 V ; $[\text{NaCl}]_0 = 0.5 \text{ mol dm}^{-3}$; Pt-Pt electrodes; Temp.: 35°C .

Table 2. Values of chemical oxygen demand (COD) and biological degradability (BD) at certain times of EPTC electrolysis

| Electr. time/min | COD / mg dm ⁻³ | BD/% | Appl. el. charge/C |
|------------------|---------------------------|------|--------------------|
| 0 (initial) | 300 | 11 | — |
| 5 | 255 | 18 | 60.4 |
| 13 | 220 | 26 | 121.84 |
| 15 | 195 | 32 | 137.20 |
| 20 | 173 | 40 | 175.6 |
| 30 | 144 | 51 | 252.40 |

Initial conc. of EPTC = 5.3×10^{-5} mol dm⁻³; [NaCl]₀ = 0.5 mol dm⁻³, pH = 10.0, Pot. = 1.35 V, Pt–Pt electrodes.

displayed a similar rate of destruction over time both in electrochemical treatment and in homogeneous hypochlorination (Figure 1a, b), the effect of pH on VSO destruction was examined in homogeneous hypochlorination with the application of synthesised Vernolate-sulphoxide (VSO). Table 3 shows the rate coefficients of the pseudo-first order reaction in the case of different starting pH values and also shows the $A_{\text{HClO}}/A_{\text{ClO}^-}$ ratio calculated from UV spectrophotometric measurements of HClO (236 nm) and ClO⁻ (292 nm) UV absorbances.

It can be seen that the rate of VSO destruction can be increased by reducing pH values, but at the same time Figure 2a–c indicates that a pH decrease is unfavourable for sulphoxide production. So UV light effect was also examined because it was successfully applied in a diluted, 5–10 ppm solution in the UV photocatalytic destruction of thiocarbamates [8].

Figure 5 shows VSO concentration changes in time in the hypochlorous oxidation of Vernolate both with and without UV light (Mercury lamp) irradiation. UV irradiation considerably increased the rates of VSO production and destruction, so it was examined whether it also affects the electrochemical destruction of Vernolate.

Electrolysis was performed in a quartz cell with Pt–Pt electrodes under identical reaction conditions. Spectra were recorded with diode array spectrophotometer with the electrolyte being circulated through a flow quartz cuvette.

Table 4 gives solution UV absorbance values at the same reaction times in electrolysis performed with and without UV light irradiation.

Table 3. Pseudo-first-order rate constants of hypochlorination of Vernolate-sulphoxide (VSO) as a function of initial pH and of the HClO/ClO⁻ UV absorptivity (A) ratio at 25 °C

| pH | $A_{\text{HClO}}/A_{\text{ClO}^-}$ | k_1/s^{-1} | k_1/s^{-1} Stand. Dev. |
|------|------------------------------------|-----------------------|---------------------------|
| 4.40 | 3.54 | 6.53×10^{-2} | $\pm 0.16 \times 10^{-2}$ |
| 6.01 | 2.84 | 1.84×10^{-2} | $\pm 0.07 \times 10^{-2}$ |
| 8.00 | 0.19 | 6.81×10^{-4} | $\pm 0.19 \times 10^{-4}$ |

[VSO]₀ = 4.82×10^{-4} mol dm⁻³; Free available [Cl₂]₀ = 2.25×10^{-3} mol dm⁻³, [Cl⁻]₀ = 0.5×10^{-3} mol dm⁻³. The individual UV absorptivity (A) of HClO and ClO⁻ at each initial pH was experimentally determined.

The first part (from 10th to 100th s) of the reactions was investigated using spectrophotometric measurement with calibration. Each k_1 value is the average of two measurements.

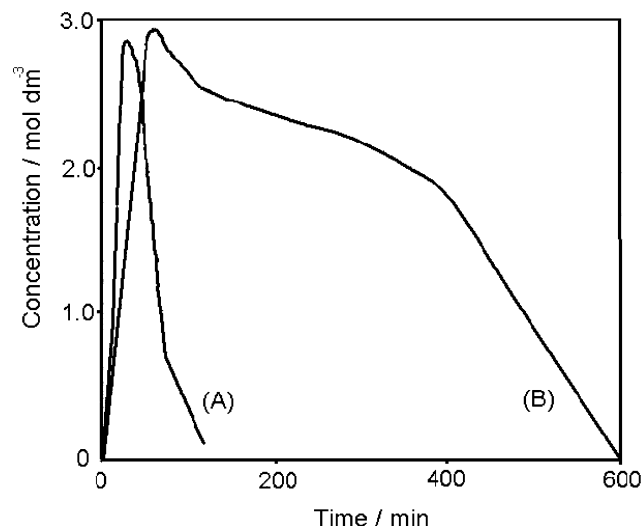


Fig. 5. Change of concentration of Vernolate-sulphoxide (VSO) in time at hypochlorous oxidation of Vernolate influenced with UV (125 W Mercury-lamp) irradiation (A) and without UV irradiation (B). Initial Vernolate conc.: 4.7×10^{-5} mol dm⁻³; Free available [Cl₂]₀ = 2.2×10^{-4} mol dm⁻³; pH = 7; Temp.: 35 °C.

Table 4. Values of UV absorbances of the solution in the electrolysis of Vernolate with and without UV irradiation at certain times of electrolysis

| Reaction time /s | Appl. el. charge /C | UV absorbance at 214 nm | |
|------------------|---------------------|-------------------------|---------------------|
| | | Without UV irradiation | With UV irradiation |
| 0 (initial) | | 2.320 | 2.320 |
| 30 | 330 | 2.063 | 1.457 |
| 60 | 660 | 1.963 | 0.971 |

Initial conc. of Vernolate: 4.7×10^{-5} mol dm⁻³, [NaCl]₀ = 0.5 mol dm⁻³, pH = 9.04; Pot. = 1.41 V; Pt–Pt electrodes, 125 W Mercury-lamp, Temp.: 35 °C.

According to data in Table 4, UV light also accelerates Vernolate destruction in electrolysis in alkaline medium, with the destruction leading through VSO intermediate to complete mineralisation. This occurs especially if the electrochemical destruction of thiocarbamates (which involves thiocarbamate-sulphoxide production) is started in alkaline medium, but sulphoxide destruction is concluded in neutral or slightly acidic medium.

4. Conclusion

In NaCl solutions the electrochemical destruction of the active ingredient thiocarbamate, and the production and degradation of intermediates appear to proceed much in the same fashion as their hypochlorous destruction. This is due to the effect of water–chlorine equilibrium. The destruction of the thiocarbamate “mother compound” is much faster in acidic or slightly acidic (Cl₂ or HOCl domains) medium than in alkaline (ClO⁻ domain) conditions.

In every domain of $\text{Cl}_2\text{-H}_2\text{O}$ equilibrium, the thiocarbamate "mother compound" degrades much faster in electrolysis than the intermediates produced from it. In different domains different intermediates are produced but there are also intermediates present in every range in different concentrations.

In ClO^- domain (with alkaline pH) mainly oxidation intermediates are produced, while in strongly or slightly acidic medium (in Cl_2 and HOCl domains) mainly chlorinated intermediates are produced.

The degradation of oxidation intermediates (e.g. VSO) produced during thiocarbamate destruction is faster than that of chlorinated intermediates. The complete reduction of TOC content and the complete mineralisation of the contaminated wastewater solution can only be achieved in ClO^- domain. UV irradiation accelerates the electrochemical destruction of thiocarbamate herbicides and their degradation intermediates.

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