Halo-organic pollutants: The effect of an electrical bias on their decomposition mechanism on porous iron electrodes

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ABSTRACT

The de-halogenation processes of $CH_2BrCHBrCOO^-$ and of $CH_2ClCH(OH)COO^-$ on Zero Valent Iron (ZVI) powders and porous iron electrodes were studied. The results suggest that by applying a negative voltage bias on the electrode, the composition of the products obtained is dramatically changed. Furthermore, the applied potential inhibits the passivation of the ZVI. Thus, it is recommended that the application of a negative potential to porous ZVI is desirable in batch treatment of halo-organic pollutants.

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1. Introduction

Halo-organic compounds are major environmental pollutants [1]. The halogen substituents can increase the hydrophobicity of organic compounds, increasing their tendency to become bio-accumulated in the food chain as well as absorbed by soil. See for example the following recent reviews (references [1–9]). Pollution caused by anthropogenic halogenated organic compounds is a serious environmental problem for decades [10–13]. Most of the top hundred species in the List of Hazardous Compounds [14] are halogenated compounds (including chlorinated and brominated organic compounds) [15,16]. Large quantities of chlorinated organic molecules cause environmental pollution as a result of their widespread use as herbicides, insecticides, fungicides, solvents, hydraulic and heat-transfer fluids, plasticizers, cleaning agents, fumigants, aerosol propellants, gasoline additives, degreasers and intermediates for chemical syntheses [17]. De-halogenation reactions are involved in synthetic chemistry [18,19] and in the decomposition reactions of halogenated pol-

lutants [20–27]. Halo-organic compounds, mainly chloro- and bromo-organic, are produced in large scale as solvents, pesticides, raw materials for organic synthesis and flame-retardants [28]. Hence, the importance of the research on the reduction mechanisms of these compounds and the substitution of the halogen atoms by less harmful substituents.

Zero Valent Iron (ZVI) is one of the most efficient de-halogenation agents and is widely used both in treating polluted underground water streams and in industrial batch processes. See for example the following recent reviews [29–36]. ZVI has been known for its hazardous waste removal ability since the seminal works of Gillham and O'Hannesin [29] as well as Matheson and Tratnyek in 1994 [30]. Two mechanisms are involved in the de-halogenation processes induced by ZVI:
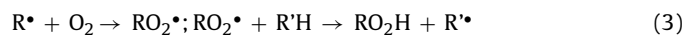
I. Direct dehalogenation:

$$Fe^\circ + 2RX \rightarrow Fe^{II}_{aq} + 2R^\cdot + 2X^- \tag{1}$$

II. *Via* oxidation of the organic substrate in a mechanism involving the Fenton reaction [34,35]:

$$Fe^\circ + O_2 + 2H^+ \rightarrow Fe^{II}_{aq} + H_2O_2 \tag{2}$$
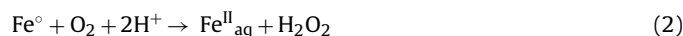
Followed by the reaction of Fe^{II}_{aq} with H_2O_2 or with other peroxides formed in the process, *e.g.* via:

$$R^\bullet + O_2 \rightarrow RO_2^\bullet;\ RO_2^\bullet + R'H \rightarrow RO_2H + R'^\bullet \tag{3}$$
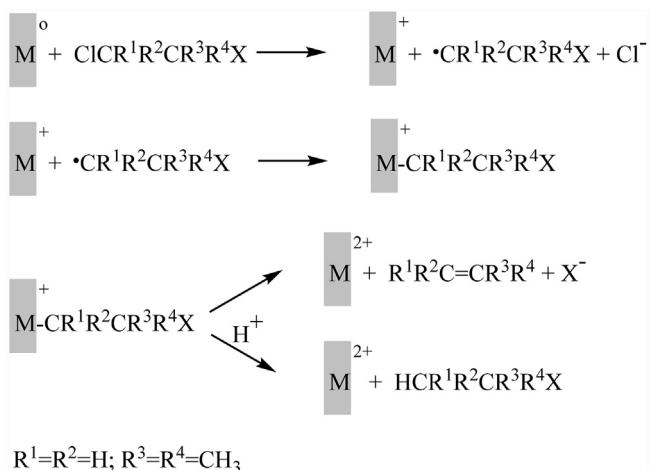
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$$M^o + ClCR^1R^2CR^3R^4X \longrightarrow M^+ + {}^{\bullet}CR^1R^2CR^3R^4X + Cl^-$$

$$M^+ + {}^{\bullet}CR^1R^2CR^3R^4X \longrightarrow M\text{-}CR^1R^2CR^3R^4X$$

$$M^+\text{-}CR^1R^2CR^3R^4X \xrightarrow{H^+} \begin{cases} M^{2+} + R^1R^2C{=}CR^3R^4 + X^- \\ M^{2+} + HCR^1R^2CR^3R^4X \end{cases}$$

$$R^1 = R^2 = H; \quad R^3 = R^4 = CH_3$$

Scheme 1. Mechanism for the de-halogenation of halo-organic compounds, good leaving groups (X), on the β position, on metal surfaces [42]. Adapted with permission from Ref. [42]. Copyright (2006) American Chemical Society.

It is commonly assumed that OH• radicals are formed in the Fenton and Fenton like reactions. However, recent results, mainly in non-acidic solutions, point out that this is not always the case [37–41].

On the other hand, the application of ZVI has several drawbacks as listed in the review by Dong et al. [36]:

a The surface area of permeable iron membranes is relatively small, a difficulty that can be overcome using Fe°-nano-particles.
b The surface of ZVI is covered by Fe$^{III/II}$-hydroxides/oxides due to corrosion. This cover increases due to the reduction of the pollutants.
c Due to the formation of Fe$^{III/II}$-hydroxides/oxides the application of ZVI is preferable in slightly acidic solutions. However, in practice work in neutral solutions is needed.

The metal-surface de-halogenation mechanism of some halo-organic compounds, containing good leaving groups on the β position to the halogen substituent (in which the formation of the following radicals is expected: •CH$_2$CH$_2$NH$_3^+$, •CH$_2$C(CH$_3$)$_2$OH, •CH$_2$CH(CH$_3$)OH and •CH$_2$CH$_2$OH) was studied [42]. The metal powders investigated were Ni°, Co° and Fe°. The results indicated that the mechanism of these de-halogenations is as follows in Scheme 1 [42]:

(Note: the metal particles consist of M° atoms, the charge on the particle is a charge delocalized on the entire particle or on one atom on the surface. Hence, it appears in the text as (M°)$^{2+/+}$-R).

The first reaction in this scheme suggests that the radicals, R•, are the first short-lived intermediates formed in the de-halogenation processes. As these radicals are formed in the vicinity of the metal surface and as the reactions of radicals with metals are very fast [43–48], the second reaction is clearly an essential part of the de-halogenation process. These reactions have very high rate constants, probably due to the fact that the electrons in the conduction band behave as radicals and react therefore with other radicals [49]. The properties of the transients (M°)$^+$-CR^{1}R^{2}CR^{3}R^{4}X formed in the second reaction in the scheme depend on the nature of M and on the nature of the substituents R^i and X [42]. The mechanisms of decomposition of the (M°)$^+$-CR^{1}R^{2}CR^{3}R^{4}X transients depend also on the pH of the aqueous medium, on the temperature and probably on the nature and concentration of plausible substrates present in the medium. The transients (M°)$^+$-CR^{1}R^{2}CR^{3}R^{4}X might in principle decompose also via homolytic decomposition of the M—C bond and/or via reaction with substrates present in the medium.

However, the latter reactions were as of yet not reported. The characteristics of the substrate molecule and reaction conditions will determine the main products of the de-halogenation process.

In many organic-electrochemical processes transient radicals and radical-ions are formed. For example, during oxidation of RCO$_2^-$ in the Kolbe reaction [50–52], the primary radical RCO$_2^{\bullet}$ decomposes into R$^{\bullet}$ + CO$_2$ and the nature of the final products is the result of reactions of the R$^{\bullet}$ radicals. As radical formation in electrochemical reactions occurs in the vicinity of the electrode, they often react with the electrode [53–58]. The mechanisms of decomposition of the transients thus formed often depend on the potential applied in the electrochemical process [53,59].

Thus for example the mechanism of the electrochemical de-halogenation of 1,4-dibromobutane in dimethylformamide (DMF) depends on the applied cathodic potential [50]. The products mixture obtained may only be explained in terms of a transient consisting of a radical bound to the metallic electrode. Reduction of diazonium salts on electrode surfaces produces either an intermediate or a stable product with a covalent bond between an organic residue and the metallic electrode [55,60–63]. Similar reactions were observed on conductor and semi-conductor surfaces [54,61,64–66]. Also, the initiation stage in the production of organo-metallic compounds through electrochemical reactions with metals such as Pd, Cd and Hg involves the formation of transients with M—C σ bonds [56]. The formation of σ bonds between radicals and other metal surfaces as well as semi-conductors and metal oxides surfaces was also reported [43–49,67–72].

It was reported that the reduction of CCl$_4$ on an iron electrode surface, under an electrical bias, yields CH$_4$ and that no intermediates, e.g. CHCl$_3$, CH$_2$Cl$_2$ or CH$_3$Cl, are observed [20]. On the other hand, it was reported that the reduction of CHCl$_3$ on an iron surface electrode occurs at a slower rate compared to CCl$_4$ [73,74]. The latter observation is in accord with the report that the de-chlorination of CCl$_4$ with iron powder does not produce CH$_4$ [67]. This apparent discrepancy was clarified by the report that the products of de-halogenation of CCl$_3$CO$_2^-$ on a porous iron electrode depend on the negative voltage bias applied on the electrode [59].

Thus, applying a constant electrical bias on a metallic electrode at potentials that do not induce faradaic currents may affect the cleavage mechanisms of the transients having metal-carbon σ bonds as well as on the final products. The applied potential bias has an additional advantage: it inhibits the formation of the Fe$^{III/II}$-hydroxides/oxides and thus accelerates the de-halogenation process. Therefore, it was decided to study the de-halogenation reactions of 2,3-dibromo-propionate and 2-hydroxyl-3-chloro-propionate on an iron powder surface at room temperature. This study focused on: (1) the de-halogenation mechanism of the halo-organic compounds performed on an iron powder surface and on porous iron electrodes; (2) the influence of the electrical bias applied on porous electrodes on the efficiency of the de-halogenation processes and on their mechanisms. Understanding these mechanisms may contribute to the development of new and efficient de-halogenation processes.

2. Experimental section

2.1. Materials

All chemicals used were of analytical purity level and purchased from Sigma-Aldrich, Merck, J.T. Baker and Frutarom. Iron powder, particle size ≤10 μm and 99% purity, was purchased from Merck. The water used was de-ionized and further purified by a Millipore Milli-Q system, achieving a final resistance of >15 MΩ cm. The inorganic gases were of analytical purity level and purchased from