

Electroreductive dechlorination of α -hexachlorocyclohexane catalyzed by iron porphyrins in nonaqueous media

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ABSTRACT: Two iron porphyrins, (TPP)FeCl and (OEP)FeCl, where TPP and OEP are the dianions of tetraphenylporphyrin and octaethylporphyrin, respectively, were utilized as catalysts for the electroreductive dechlorination of α -hexachlorocyclohexane (α -HCH) which was monitored by electrochemistry, *in situ* UV-visible spectroelectrochemistry and controlled potential electrolysis in N,N'-dimethylformamide. GC-MS analysis of the α -HCH degradation products revealed the stepwise formation of pentachlorocyclohexene and tetrachlorocyclohexadiene as intermediates, prior to generation of the final dechlorination products which consisted of an isomeric mixture of trichlorobenzenes. Based on identification of the intermediates and final products in the reaction, an overall dechlorination mechanism of α -hexachlorocyclohexane is proposed.

KEYWORDS: iron porphyrins, α-hexachlorocyclohexane, reductive dechlorination, electrochemistry, spectroelectrochemistry, electrocatalysis.

INTRODUCTION

Technical grade hexachlorocyclohexane (HCH), which is sold as a mixture of isomers containing 55–80% of α -HCH, 5–14% of β -HCH, 8–15% of γ -HCH, 2–16% δ -HCH, and 3–5% ϵ -HCH [1], was extensively used as a pesticide during the latter half of the 20th century [2]. Only the γ -HCH isomer, known as lindane, has specific insecticidal activity, but the less expensive technical grade HCH continued to be used in developing countries for the economic reasons [1, 3]. However, due to their known damage to ecosystems and human health, the α , β and γ isomers of HCH were listed in 2009 as persistent organic pollutants (POPs) by the Stockholm Convention [4].

Many groups have investigated the chemical and biological properties of HCH and their effect on the environment and human health. For example, Pućko et al. studied the effect of zooplankton seasonal migrations on α -HCH bioaccumulation [5] and described the mechanisms and implications of α -HCH enrichment in melt ponds formed from ice during the summer in the Canadian high Arctic [6]. Xu et al. evaluated the carcinogenic risk of HCHs in the muscles of fish from Lake Baiyangdian, China [7]. The residue levels of HCH in sediments from the middle and lower reaches of the Yellow River, China and its tributaries were investigated by Wang et al. [8]. Fabre et al. proposed analytical procedures for determination of the different HCH isomers present in vegetables, human and animal tissues, blood and serum [9]. Liu et al. explored the residue status, factors influencing the distribution patterns, enantiomeric signature of α -HCH and potential human exposure risks of HCHs in agricultural soils in China [10]. Xu et al. propsed the air-water exchange direction of HCHs in the water phase [11]. Dachs et al. reported the concentrations of HCHs and other POPs in seawater and phytoplankton from the Southern Ocean [12].

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Moreover, with the aim of protecting humans and the environment from pollution with HCH, several disposal and remediation techniques have been extensively studied. Ukisu *et al.* reported that HCH isomers could be dechlorinated to give benzene in the presence of alkaline 2-propanol and a supported palladium catalyst (Pd/C) [13]. Esteruelas *et al.* used rhodium and ruthenium complexes to catalyze the dechlorination of HCH to benzene or cyclohexene [14]. Various final degradation products of γ -HCH, such as benzene, chlorobenzene or cyclohexane, were reported when the zero-valent iron, Fe-Pd or Pd/ Fe⁰ nanoparticles were used as catalysts [15–17]. Additional research has focused on the biodegradation of HCH isomers and different processes and mechanisms for dechlorination were also investigated [18-25]. The electrochemical dechlorination of HCH isomers has also been proposed [26-29].

Several porphyrins and phthalocyanines containing transition metal ions have been applied to catalyze the reductive dehalogenation of organohalides [30-32]. Our own group recently reported the use of manganese, cobalt and iron porphyrins as catalysts for the electroreduction of 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) in N,N'-dimethylformamide (DMF) [33-35]. In the

(a) Iron porphyrins

present study, two iron porphyrins were utilized as catalysts for the electrochemical reduction of α -HCH in DMF. The α -HCH isomer was chosen to study in the present work because it is the most abundant isomer in the environment. The utilized porphyrin catalysts were (Por) FeCl where Por = the dianion of tetraphenylporphyrin (TPP) or octaethylporphyrin (OEP). The structures of these macrocycles are shown in Chart 1, along with the structures of α -HCH and its dechlorination products as determined in the current study.

RESULTS AND DISCUSSION

Cyclic voltammograms of (Por)FeCl in the absence and presence of α-HCH

(TPP)FeCl and (OEP)FeCl both undergo three reversible one-electron reductions in DMF containing 0.1 M TBAP as supporting electrolyte. Examples of cyclic voltammograms are shown by the solid lines in Fig. 1. The half-wave potentials corresponding to these electron transfer processes are located at $E_{1/2} = -0.16$, -1.02 and -1.65 V for (TPP)Fe^{III}Cl and $E_{1/2}$ = -0.29, -1.24







Chart 1. Structures of investigated iron porphyrins, as well as α -HCH and its dechlorination products



Fig. 1. Cyclic voltammograms of (a) (TPP)FeCl $(5.0 \times 10^{-4} \text{ M})$ and (b) (OEP)FeCl $(5.0 \times 10^{-4} \text{ M})$ in DMF containing 0.1 M TBAP before (—) and after (- -) addition 1.0 equivalents α -HCH to solution. Scan rate = 0.1 V/s

and -1.94 V for (OEP)Fe^{III}Cl. Similar electrochemical behavior has previously been reported for other related iron porphyrins in nonaqueous media [36, 37].

The first reduction of (Por)Fe^{III}Cl generates an Fe(II) porphyrin and this is followed at more negative potentials by generation of an Fe(I) porphyrin π -anion radical and Fe(I) porphyrin dianion as shown in Equation 1 [37].

$$(Por)Fe^{II}Cl+ e \rightleftharpoons (Por)Fe^{II} + Cl^{-}$$
(1a)

$$(Por)Fe^{II} + e \rightleftharpoons [(Por)Fe^{I}]^{-}$$
(1b)

 $[(Por)Fe^{I}]^{-} + e \rightleftharpoons [(Por)Fe^{I}]^{2}$ (1c)

The first reduction of (TPP)FeCl and (OEP)FeCl remains reversible in DMF after 1.0 equivalent α-HCH has been added to solution. These cyclic voltammograms are shown by the dashed lines in Figs 1a and 1b. The second reduction of (TPP)FeCl also remains reversible in DMF containing 1.0 equivalent α -HCH, although a higher cathodic current is observed than in the absence of HCH. In contrast, the second reduction of (OEP)FeCl is totally irreversible in DMF containing 1.0 equivalent α -HCH and this process exhibits a much increased peak current, which increases even further as the concentration of α -HCH added to the DMF solution is increased above 1.0 equivalent. The electrochemical behavior indicates the lack of a reaction between α -HCH and the neutral Fe(III) or singly reduced Fe(II) forms of the two porphyrins. This is not the case for the electrogenerated Fe(I) porphyrins which react with the added α -HCH in DMF. The chemical reaction is slower for $[(TPP)Fe^{I}]^{-}$ than for $[(OEP)Fe^{I}]^{-}$ as evidenced by the almost reversible second reduction of (TPP)FeCl in DMF containing 1.0 equivalent α -HCH



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Fig. 2. Plots of I_p/I_p vs. the ratio of (a) [α -HCH]/[(TPP)FeCl] and (b) [α -HCH]/[(OEP)FeCl] in DMF, 0.1 M TBAP

at a scan rate of 0.1 V/s. The irreversible processes and increased peak currents in solutions of (TPP)FeCl or (OEP)FeCl with higher concentrations of α -HCH is consistent with homogeneous reactions involving α -HCH (R-Cl) and [(Por)Fe¹]⁻ or [(Por)Fe¹]²⁻ to form σ -alkylmetal porphyrins at the electrode surface [38, 39].

The changes in maximum peak current for the first two reductions of (Por)FeCl were examined as a function of increasing α -HCH concentration by constructing plots of I_p/I_p vs. the ratio of [α -HCH]/[(Por)FeCl]. Examples of these plots are shown in Fig. 2, where $I_{n'}$ and I_{n} are the measured cathodic peak currents obtained from the cyclic voltammograms for reduction in the presence and absence of α -HCH, respectively. The I_p/I_p ratio is unchanged with increase in the concentration of α -HCH during the first reduction (Fe^{III}/Fe^{II} process) of (TPP)FeCl (Fig. 2a) or (OEP)FeCl (Fig. 2b), consistent with the fact that neither the Fe(III) nor the Fe(II) porphyrin reacts with α -HCH. However, the values of I_p/I_p for the second reduction of (TPP)FeCl and (OEP)FeCl both increase as the ratio of the $[\alpha$ -HCH]/[(Por)FeCl] concentration is increased, implying that the Fe(I) forms of (TPP)FeCl or (OEP)FeCl will react with α -HCH under the given solution conditions. The fastest reaction occurs with (OEP)FeCl where the ratio of peak currents has increased more than five times in DMF containing 1.0 equivalent α -HCH while in the case of (TPP)FeCl, the peak current has increased by only a little more than 50% under the same solution conditions.

The increase in current at potentials for the second and third reductions of (Por)FeCl is not due to the direct reduction of α -HCH, since no reductions are seen for this compound in DMF containing 0.1 M TBAP between 0.0 and -2.0 V vs. SCE. An electroreduction of γ -HCH has been reported at -2.16 V vs. SCE in DMF containing 0.1 M TBABF₄ [27, 28], but this potential is beyond that for the catalytic reductions illustrated in Fig. 1. Therefore, the increased peak currents observed during the last two reductions of (Por)FeCl in DMF containing α -HCH are generated from a catalytic reduction which occurs between the Fe(I) porphyrins and α -HCH.

Spectroelectrochemical monitoring of (Por)FeCl reductions in DMF with and without added α-HCH

In a previous study, *in situ* UV-visible spectroelectrochemistry was utilized to monitor the products of a chemical reaction involving α -HCH and electrogenerated cobalt, manganese or iron metalloporphyrins [33–35]. Spectroelectrochemistry is also used in the current study to monitor the reductions of (Por)FeCl in DMF with and without added α -HCH. Examples of the spectral changes which occur during the first two reductions of (TPP)FeCl in the absence and presence of α -HCH are shown in Fig. 3.

Identical spectral changes are observed during the first one-electron reduction of (TPP)FeCl in DMF with and without added α -HCH (Fig. 3a). This result confirms that

Fe(II) does not react with α -HCH under the given solution conditions. However, the spectral changes obtained during the second reduction of (TPP)FeCl in the absence of α -HCH differs from what is seen in the presence of α -HCH (Fig. 3b). The final spectrum after reduction at -1.40 V in DMF without α -HCH exhibits a split Soret band at 396 and 427 nm, both of which are characteristic of an Fe(I) tetraphenylporphyrin [40]. This spectral pattern is not observed after the second reduction of (TPP)FeCl in DMF solutions containing α -HCH (Fig. 3b). In this case, the final UV-visible spectrum displays a singly intense Soret band at 440 nm (Fig. 3b). A similar spectrum has been reported for related σ -bonded Fe(III) porphyrin with TPP macrocycle where the Soret band maximum ranges from 408 to 440 nm [39, 41].

The spectroelectrochemical data in Fig. 3 is thus consistent with the cyclic voltammetric data in Fig. 1 in that a catalytic reaction involving α -HCH and the electrogenerated Fe(I) porphyrin occurs after the second reduction in DMF containing added α -HCH.

Controlled-potential bulk-electrolysis

To determine the dechlorination products of α -HCH, controlled-potential bulk electrolysis was carried out in DMF solutions containing 2.0×10^{-4} M (Por)FeCl and 2.0×10^{-3} M α -HCH. The potentials applied for bulk electrolysis were set at -1.40 V for (TPP)FeCl and -1.50 V for (OEP)FeCl. Both potentials are sufficiently negative to generate the Fe(I) form of the porphyrin and also to reduce any homogeneously generated σ -bonded Fe(III) porphyrin products [36]. Figure 4 illustrates GC analysis



Fig. 3. Thin-layer UV-visible spectral changes of (TPP)FeCl during (a) the first and (b) second one-electron reductions in DMF containing 0.1 M TBAP with and without added 5 equivalents α -HCH



Fig. 4. GC analysis of α -HCH and its dechlorinated products in DMF at different controlled-potential electrolysis times

of α -HCH and its dechlorinated products in DMF for controlled-potential electrolysis times of 1–8 h. As seen in this figure, five main α -HCH dechlorinated products (PCCH, TCDN, 1,2,4-TCB, 1,2,3-TCB and 1,3,5-TCB) are detected after 3–5 h of electrolysis when using (TPP) FeCl as the catalyst and 2–4 h of electrolysis when (OEP)FeCl was used as catalyst. However, only three TCB isomers (1,2,4-TCB, 1,2,3-TCB and 1,3,5-TCB, see Chart 1) are seen after 6–8 h of bulk electrolysis for (OEP)FeCl and (TPP)FeCl, respectively. The calculated distribution (mol%) of α -HCH and its dechlorinated products which as a function of electrolysis time are summarized in Table 1 and plotted in Fig. 5.

As seen in this table and Figs 4 and 5, the conversion of α -HCH to the less-chlorinated compounds depends on the time. For example, pentachlorocyclohexene (PCCH) increases in abundance at the start of electrolysis, but declines as the electrolysis proceeds. Identification of the final dechlorinated products of α -HCH are the three trichlorobenzene isomers (1,2,3-TCB, 1,2,4-TCB and 1,3,5-TCB) are based on an real sample and GC-mass spectrum. Two intermediates are proposed to be PCCH



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Fig. 5. The distribution of α -HCH and its products obtained in DMF at different electrolysis times during controlled-potential reduction of (a) (TPP)FeCl at -1.40 V and (b) (OEP)FeCl at -1.50 V

and tetrachlorocyclohexadiene (TCDN), but it should be noted that authentic samples of PCCH and TCDN are not commercially available. Other less dechlorinated products like di- or monochlorobenzene or benzene were not detected even after longer electrolysis time in these experiments.

The data in Table 1 indicates that the dechlorination efficiency of α -HCH is affected by the structure of the catalysts, either (TPP)FeCl or (OEP)FeCl. When (TPP) FeCl is used as the catalyst, α -HCH was 100% mono-dechlorinated after 6 h of controlled-potential electrolysis while only 4 h are needed to totally convert a α -HCH to the less dechlorinated products using (OEP)FeCl. In addition, 8 h are needed for α -HCH to be completely degraded to form TCB when using (TPP)FeCl as the catalyst as compared to 6 h in the case of (OEP)FeCl. Thus, (OEP)FeCl is a better electrocatalyst for the reductive dechlorination of α -HCH as compared to (TPP)FeCl under the same solution conditions.

Proposed mechanism for dechlorination of α-HCH

A proposed catalytic cycle for the reductive dechlorination of α -HCH is illustrated in Scheme 1 based on the

Catalyst	Electrolysis time, h	Distribution, mol% ^a					
		α-НСН	РССН	TCDN	1,2,4-TCB	1,2,3-TCB	1,3,5-TCB
(TPP)FeCl	0	100	0.0	0.0	0.0	0.0	0.0
	1	83.3	10.2	6.4	0.0	0.0	0.0
	2	60.8	16.4	10.1	6.8	4.6	1.4
	3	35.2	21.5	15.3	15.3	9.2	3.6
	4	20.4	25.7	11.2	23.7	12.4	6.6
	5	8.1	24.9	5.2	34.2	17.4	10.3
	6	0.0	13.3	1.1	45.6	26.8	13.3
	7	0.0	6.2	0.0	49.8	28.5	15.6
	8	0.0	0.0	0.0	51.9	29.3	18.8
(OEP)FeCl	0	100	0.0	0.0	0.0	0.0	0.0
	1	56.9	16.7	5.4	11.5	6.4	3.1
	2	29.0	20.4	14.8	18.6	11.5	5.7
	3	10.3	23.0	8.4	30.1	18.7	9.6
	4	0.0	12.9	3.7	45.4	23.4	14.5
	5	0.0	5.7	0.0	48.2	27.4	18.7
	6	0.0	0.0	0.0	50.8	28.5	20.7

Table 1. Analysis data of α -HCH and its dechlorinated products at different reaction time during the controlled-potential electrolysis at -1.40 V for (TPP)FeCl and -1.50 V for (OEP)FeCl in DMF

^a Distribution (%) = [(moles of a specific compound)/(moles of all compounds)] $\times 100\%$.

electrochemistry, spectroelectrochemistry and GC-MS analysis. Neutral (Por)Fe^{III}Cl initially undergoes two stepwise one-electron reductions to yield the corresponding Fe(I) porphyrin which then reacts with α -HCH to generate the organometallic intermediate having an Fe–C σ -bond, (Por)Fe–(R). This Fe(III) intermediate is further reduced and undergoes a cleavage of the Fe–C bond leading to the Fe(II) porphyrin with the subsequent stepwise generation of PCCH, TCDN and then TCB.

The formation of (Por)Fe-(R) is a nucleophilic substitution process with the tendency of the reaction depending on the R-Cl bond energy and the nucleophilicity of [(Por)Fe¹]. The nucleophilicity [(OEP)Fe¹]. is stronger anionic nucleophile than [(TPP)Fe^I]⁻ due to different substituents [36]. Thus, (OEP)FeCl has a higher catalytic efficiency than (TPP)FeCl in the process involving dechlorination of α -HCH. However, this does not mean that any iron porphyrin with a higher electron density on the macrocycle can be a better catalyst for the dechlorination of α -HCH. This is because higher electron density on the macrocycle will result in the porphyrin being more difficult to be reduced to form the reactive Fe(I) species. In the extreme case, if the potential for generating the Fe(I) porphyrin becomes too negative then, α -HCH would be directly electroreduced at the same time for a formation of an Fe(I) porphyrin and there could be no need for a catalyst.

EXPERIMENTAL

Chemicals

Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemical Company and recrystallized prior to use. N,N'-dimethylformamide (DMF) was purchased from Shanghai Sinopharm Chemical Reagent Co. (SCRC) and freshly distilled before use. The iron porphyrins (TPP)FeCl and (OEP)FeCl were purchased from Sigma-Aldrich, α -hexachlorocyclohexane (α -HCH) was purchased from Shanghai Anpel Scientific Instrument Co. and the TCBs (1,2,3-TCB, 1,2,4-TCB, 1,3,5-TCB) were purchased from SCRC. All the iron porphyrins, α -HCH, TCBs and other chemicals were of high-purity grade and were used without further purification.

Instrumentation

Cyclic voltammetry was performed in a threeelectrode cell using a CHI-730D electrochemistry station. A glassy carbon disk electrode was utilized as the working electrode while a platinum wire and a saturated calomel electrode (SCE) were employed as the counter and reference electrodes, respectively. An "H" type cell with a fritted glass layer to separate the cathodic and anodic sections of the cell was used for bulk electrolysis.



Scheme 1. Proposed mechanism of electroreductive dechlorination of α -HCH to give PCCH, TCDN and TCB when catalyzed by iron porphyrins

The working and counter electrodes were made from platinum mesh and the reference electrode was an SCE. Both the working and reference electrodes were placed in one compartment while the counter electrode was in other compartment of the cell.

UV-visible spectroelectrochemical measurements were performed with a home-made optically transparent thin-layer cell with a Pt mesh as the working electrode. The potential was applied using a CHI-730D electrochemistry station. Time-resolved UV-visible spectra were recorded with an Agilent 8453A diode array spectrophotometer. All electrochemical and spectroelectrochemical measurements were carried out under a nitrogen atmosphere.

The electrolysis products were identified with the aid of gas chromatography-mass spectrometry (GC-MS); an

Agilent 6890 gas chromatograph fitted with a $30 \text{ m} \times 0.25 \text{ mm}$ DB-5MS capillary column (Agilent Corporation) in tandem with an Agilent 5975 inert mass-selective detector was employed for these measurements. After each hour of electrolysis, 1.0 mL of solution was taken from the H-cell and the supporting electrolyte removed prior to the GC-MS analysis which was carried out as described in the literature [34].

CONCLUSION

In summary, the doubly reduced (TPP)Fe^{III}Cl and (OEP)Fe^{III}Cl, which are represented as [(Por)Fe^I]⁻, can catalyze the dechlorination of α -hexachlorocyclohexane (α -HCH) to stepwise generate pentachlorocyclohexene (PCCH) and tetrachlorocyclohexadiene (TCDN) as intermediates, prior to generation of the final dechlorination products which consisted of an isomeric mixture of trichlorobenzenes (TCB). The experimental data indicate that (OEP)FeCl is a better catalyst for the reductive dechlorination of α -HCH as compared to (TPP)FeCl under the given experimental conditions.

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