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# Catalytic effects of activated carbon on hydrolysis reactions of chlorinated organic compounds
## Part 1. γ-Hexachlorocyclohexane

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## Abstract

Dehydrochlorination of γ-hexachlorocyclohexane (γ-HCH or lindane) in aqueous solution in the presence of activated carbon (AC) was studied. Hydrolysis of lindane is accelerated in the presence of AC at moderate pH values, which is ascribed to a catalytic effect of the AC in the dehydrochlorination reaction. A novel reaction pathway leading to dichlorobenzenes was found in the presence of AC, whereas the hydrolysis in homogeneous solution stops at the stage of trichlorobenzenes. The contribution of the novel pathway to the overall reaction depends on the pH value. Indications for a slow neutral hydrolysis reaction were found. Conducting the hydrolysis in AC suspension with $D_2O$/NaOD, no deuterium was found in the DCB formed, which implies that all hydrogen in the DCB originates from the parent molecule lindane. A hypothesis for the reaction mechanism is proposed.

*Keywords:* Dehydrochlorination; γ-Hexachlorocyclohexane; Activated carbon; Catalysis; Alkaline hydrolysis

## 1. Introduction

During their half-century of use, the isomers of hexachlorocyclohexane (HCH) have penetrated into almost all environmental compartments, even down to the depths of the oceans. On the basis of the former HCH application pattern, the ratio of α-HCH/γ-HCH in water masses in the North Atlantic can now be used to determine whether their place of origin is in the northern or the southern hemisphere. These observations, together with HCH concentrations in deep and groundwater, where photolysis and volatilization losses can be neglected, imply long lifetimes for HCHs [1]. The β-isomer has been determined to be recalcitrant in the environment [2]. The estimated degradation half-lives of the γ-isomer, the widely used insecticide lindane, in rivers, lakes and groundwater are 3–30, 30–300 and >300 days, respectively [3]. However, in addition to a slow biodegradation [4], lindane is accessible to alkaline hydrolysis. In aqueous environments, its dehydrochlorination follows a base-promoted β-elimination (as E2) mechanism (Eq. (1)) to the isomers of trichlorobenzene (TrCB) via γ-1,3,4,5,6-pentachlorocyclohexene (PCCHe) as intermediate [2,5]:

$$C_6H_6Cl_6 + 3OH^- \rightarrow C_6H_3Cl_3 + 3Cl^- + 3H_2O \qquad (1)$$

It was found that hydrolysis of lindane follows pseudo-first-order kinetics at constant pH values. The second-order base rate constant ($k_b$, L mol$^{-1}$ s$^{-1}$) is calculated from the pseudo-first-order rate constant ($k'$, s$^{-1}$) according to $k_b = k'/c_{OH^-}$ [1]. A number of authors provide values for $k_b$ at 20 °C in the range between 0.01 and 0.055 L mol$^{-1}$ s$^{-1}$ [1,5–7]. From the variation of $k_b$ with temperature, an activation energy of about 85 kJ mol$^{-1}$ was determined. For pH 8 and 5 °C, Ngabe et al. state that the half-life of lindane is about 42 years [1]. At pH 7 the rate constant of the neutral hydrolysis ($C_6H_6Cl_6 + H_2O$) is $3.3 \times 10^{-8}$ s$^{-1}$, which is one to two orders of magnitude higher than calculated from $k_b c_{OH^-}$. The data of Saleh et al. [8] differ to some extent from the above: these authors found that lindane hydrolysis was catalyzed by $OH^-$ and $H^+$. Neutral hydrolysis was described as relatively unimportant.

Advanced water treatment processes, and in particular those involving adsorption onto activated carbon (AC), have proved to be the most efficient and reliable method for the

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removal of aqueous-dissolved organic pesticides [9,10]. Increasingly often, pesticides are being removed in situ from environmental media, such as groundwater, by sorption onto AC barriers. There is some information in the literature concerning the adsorption of lindane on AC [11]. These studies show that AC can be used to reduce the concentration of this pesticide down to the potable level [12]. Kouras et al. [13] studied the adsorption kinetics of lindane onto powdered AC, using an empirical model to describe the experimental results kinetically. Some authors state that small amounts of lindane are more difficult to remove from natural waters with AC than other common pesticide pollutants [14,15].

The versatile adsorbent AC has numerous applications in various fields owing to its large surface area, high sorption capacity, porous structure and variable surface chemical composition. Apart from its application as a purifying agent, AC is increasingly recognized as entering into catalytic processes, in which it acts not only as a catalyst support but also directly as a catalyst for reactions such as oxidative dehydrogenation, hydrolysis of hexanitrocobaltate(III), cumene oxidation, dehydration and dehydrogenation of butane-2-ol or even hydrolysis of soya-bean oil [16,17].

Generally, partial dechlorination of polychlorinated pollutants makes them less toxic and better biodegradable. An objective of this work was the evaluation of the benefit of AC in an on-site treatment process for groundwater contaminated with lindane. It had to be investigated whether the desired alkaline decomposition of the contaminants could also be accomplished in the sorbed state. Additionally, in situ processes at an AC barrier in the aquifer would benefit from the dehydrochlorination of lindane to TrCB, which facilitates subsequent microbiological degradation processes.

## 2. Experimental

Lindane was purchased in 99%+ purity from Hockley (UK) and used as received. All other chemicals were of the highest purity grades obtainable from Merck (Germany). Granular activated carbon (Chemviron Carbon, Filtrasorb TL830) was pulverized in order to minimize the effects of abrasion and substance transport. The material has an ash content of 5.4 wt.% and an iron content of about 0.5 wt.%. No other reduction-relevant or catalytically active metals could be found (EDXRF analysis). Using nitrogen adsorption (Gemini-2370, Micromeretics), a BET surface area of $727\ m^2\ g^{-1}$, a total intra-particle pore volume of $0.46\ cm^3\ g^{-1}$ and a micropore volume of $0.27\ cm^3\ g^{-1}$ were determined for the AC sample. The point of zero charge was determined at pH 10.8–11.3 (potentiometric titration and immersion technique).

The hydrolysis studies were carried out as batch experiments; 500 mL amber screw-cap bottles equipped with Mininert® valves were used. Four hundred and fifty millilitres of buffer solution (pref. carbonate buffer) or deionized water brought to the desired pH value with NaOH or $HNO_3$ was added and the solution inertized with nitrogen. In the experiments without AC, lindane was added as ethanolic solution, resulting in starting concentrations of $5\ mg\ L^{-1}$.

In suspensions containing AC (up to $2\ g\ L^{-1}$), portions of lindane stock solution were added stepwise at 10 min time intervals, taking into consideration the sorption equilibria of lindane: each portion initially formed a water solution with maximal $5\ mg\ L^{-1}$ freely dissolved lindane. Typically, the overall lindane concentration in the slurries was $100\ mg\ L^{-1}$ (0.344 mM). The bottles were shaken well throughout the experiments (horizontal shaker, $240\ min^{-1}$) at ambient temperature ($23 \pm 2\ °C$). At appropriate intervals, 5 mL samples of solution or slurry were taken, acidified and extracted for 24 h with 2 mL $CHCl_3$ (containing $10\ mg\ L^{-1}$ toluene as internal standard). The $CHCl_3$ extracts were analyzed using a GC–MS QP 5000 (Shimadzu Corp., 30 m thin-film capillary column DB1). The progress of the reaction was also monitored by argentometric titration of the chloride formed: 5 mL slurry samples were acidified with $HNO_3$, filtered (0.45 μm PP membrane) and titrated using a Schott titration device.

A hydrolysis experiment with $D_2O$/NaOD was carried out in a 25 mL vial. All deuterated compounds were purchased from Deuchem (Germany). Initially, 0.05 mg lindane and 10 mL $D_2O$ were added, alkalized (apparent pH ~ 12) and the vial well shaken. After 1 h reaction time, 1 mL solution was extracted with 0.5 mL $CDCl_3$ and analyzed by GC–MS (sampling point 1). One hundred milligrams of activated carbon was added to the solution; the suspension was shaken overnight and an aliquot was extracted with $CDCl_3$ (+standard) and analyzed (sampling point 2). After neutralization with $D_2O$/DCl, lindane stock solution was added in small portions as described above until a concentration of nominally $100\ mg\ L^{-1}$ (0.344 mM) was reached. The so-prepared suspension was alkalized (app. pH ~ 13) and shaken for 24 h. An aliquot of the suspension was then extracted with $CDCl_3$ (+standard) and analyzed (sampling point 3). The content of deuterium in the products (DCB, TrCB) was determined from their mass spectra (intensity ratio of $M$ and $M + 1$ signals; detection limit better than 1% of $D_1$-isotopomers).

## 3. Results and discussion

An objective of the present work was to examine the hydrolysis behaviour of the pesticide lindane in the presence of AC at various pH values. In batch experiments, the rate coefficient for the alkaline hydrolysis in homogeneous solution was found to agree fairly well with literature data [1,6,7]. At solution pH values between 10 and 13, rate constants $k_b = 0.01–0.04\ L\ mol^{-1}\ s^{-1}$ were found (data not presented in detail). We observed the typical kinetics indicative of a (pseudo) first-order consecutive reaction with PCCHe as intermediate and all three isomers of TrCB as the final products.

In the presence of powdered AC, the dehydrochlorination of lindane showed higher reaction rates than in homogeneous solutions of the same pH values when pH values below 11 were chosen (Table 1). This finding was surprising because it might be expected that the heterogeneous reaction is slowed down by transport phenomena in the carbon grain. This indicates that hydrophobic pollutants sorbed at activated carbon are well accessible for the reaction with hydrophilic reaction partners such as hydroxide ions.

Fig. 1 shows that the lindane hydrolysis in the presence of activated carbon occurs faster than in homogeneous solution at pH values below 11. At about pH 11, the homogeneous reaction is so fast that transport phenomena in the heterogeneous system become rate limiting and the addition of activated carbon loses its advantage.

The heterogeneous hydrolysis reaction follows approximately a first-order kinetics. Therefore, calculating rate coefficients from observed half-lives seems to be a reasonable approach. Nevertheless, the linear dependence between log $k_{b,heterogeneous}$ and the pH value, presented in Fig. 1, is not fundamentally founded.

In addition to the TrCB known from the homogeneous reaction, isomers of dichlorobenzene (DCB) were found as products of a novel reaction pathway (see Fig. 2). TrCB themselves do not react to DCB under these conditions.

Depending on the pH value, the product distribution between DCB and TrCB changes (Fig. 3A). At lower pH values dichlorobenzene is favoured. The conversion to lesser chlorinated compounds is an environmentally benign modification. Considering the formal carbon oxidation numbers in lindane ($C^{\pm 0}$) and the products TrCB ($C^{\pm 0}$) and DCB ($C^{-1/3}$), it is obvious that during the AC-mediated reaction pathway a redox reaction must have taken place (similar to the dichloro-elimination as described by Criddle et al. for the biotic reaction of hexachloroethane to perchloroethene [18] or the reaction with FeS described by Liu et al. to the lower chlorobenzenes [20]).

The product shares of the TrCB isomers are as in homogeneous solution constant and independent of the pH value; 5% of the total amount of TrCB is accounted for by

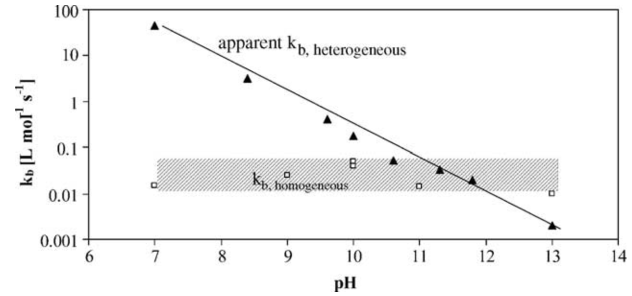

Fig. 1. Apparent base-rate coefficient of lindane hydrolysis in the presence of activated carbon at various pH values (2 g L$^{-1}$ AC, 100 mg L$^{-1}$ lindane) compared to base-rate coefficients in homogeneous solution (5 mg L$^{-1}$ lindane).

1,2,3-TrCB and 8% by 1,3,5-TrCB, but the primary TrCB isomer is 1,2,4-TrCB with a share of 87%. At constant pH values the distribution of the final products DCB and TrCB was always constant over the course of each reaction. Fig. 3B shows that the product distribution of the DCB changes with the pH value. The share of 1,3-DCB increases slightly with increasing pH value, whereas 1,4-DCB and 1,2-DCB compete against each other, whereby 1,4-DCB is favoured in acidic milieu. Fig. 3A shows clear evidence that the TrCB are the preferred hydrolysis products under alkaline conditions, whereas DCB are the dominant products of the heterogeneous reaction. Nevertheless, the heterogeneous hydrolysis reaction is affected by the pH value (Fig. 3B), either directly by involvement of hydroxide ions in the dechlorination step or indirectly by modification of the carbon surface.

For DCB formation from HCH, a reductant is necessary. We carefully excluded any reducing metal traces present in the activated carbon being responsible for the reduction. We compared original AC and HCl-leached AC under the same reaction conditions (pH 9.5, carbonate buffer, 200 mL buffer solution, nominal 100 ppm lindane, 500 mg AC). The product distribution in both samples was almost identical; however, the reaction rate in the presence of leached AC was slightly lower (which we ascribe to a partial loss of catalytic activity of the AC after the rough HCl treatment).

In order to study the contribution of water as a reaction partner, a hydrolysis experiment was carried out in $D_2O$ as solvent. If deuterated products were to be formed, reduction

Table 1
Half-lives, apparent first-order and second-order base rate coefficients for the dehydrochlorination of lindane in the presence of activated carbon at various pH values (100 mg L$^{-1}$ lindane in suspension; 2 g L$^{-1}$ activated carbon powder)

| pH value | Buffer system | $k'$ [s$^{-1}$] | $\tau_{1/2}$ (h) | $k_b$ (L mol$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|
| 7.0 | 0.01 M $NaHCO_3$; pH adjustment with HCl | $4.5 \times 10^{-6}$ | 43 | 45 |
| 8.4 | 0.01 M $NaHCO_3$ | $8.0 \times 10^{-6}$ | 24 | 3.2 |
| 9.6 | 0.01 M $NaHCO_3$/$Na_2CO_3$; pH adjustment with HCl | $1.6 \times 10^{-5}$ | 12 | 0.4 |
| 10.0 | 0.025 M $NaHCO_3$/$Na_2CO_3$ | $1.8 \times 10^{-5}$ | 11 | 0.15 |
| 10.6 | 0.01 M $NaHCO_3$/$Na_2CO_3$; pH adjustment with NaOH | $2 \times 10^{-5}$ | 9 | 0.05 |
| 11.3 | 0.01 M $NaHCO_3$/$Na_2CO_3$; pH adjustment with NaOH | $6.6 \times 10^{-5}$ | 3 | 0.03 |
| 11.8 | 0.01 M $NaHCO_3$/$Na_2CO_3$; pH adjustment with NaOH | $1.3 \times 10^{-4}$ | 1.5 | 0.02 |
| 13.0 | 0.1 M NaOH | $2 \times 10^{-4}$ | 1 | 0.002 |

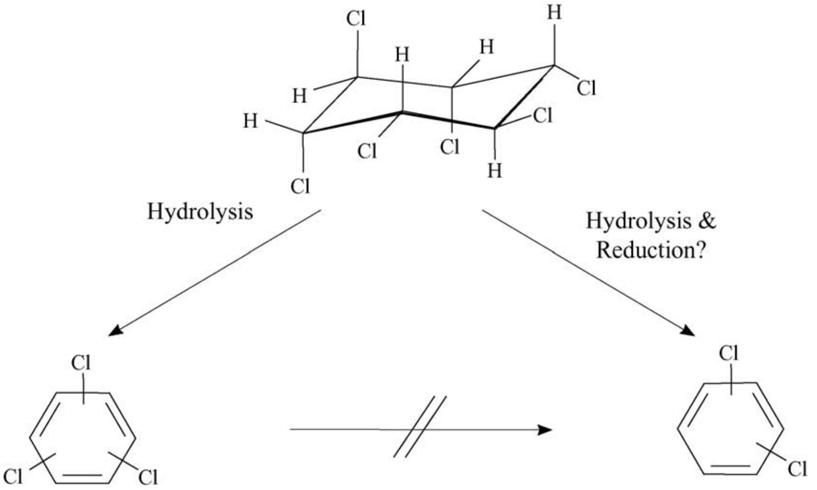

Fig. 2. Reaction pathways of lindane dechlorination in aqueous suspension in the presence of activated carbon.

equivalents for the formation of DCB would have originated from a (AC-mediated) hydride shift from the solvent, whereas the absence of deuterated products would imply that AC is the reaction partner. First, lindane was treated in alkaline $D_2O$ solution (apparent pH ~ 12) and an aliquot extracted and analyzed. The TrCB formed were free of deuterium. AC was then added; 15 h were allowed for equilibration of the system. Again, the TrCB extracted from a suspension aliquot were found to be free of deuterium. In the last step, the AC suspension was neutralized with $D_2O$/DCl and fresh lindane was added in small portions until a total concentration of 100 mg $L^{-1}$ (0.344 mM) was reached. After alkalization (apparent pH ~ 12) with $D_2O$/NaOD, the suspension was shaken for 24 h and extracted with $CDCl_3$. The TrCB and DCB formed were found to be completely free of deuterium. Thus, water is not involved in any D-transfer reaction to the chlorobenzenes under the applied conditions. On the contrary, we can conclude that the redox reaction takes place with direct participation of the activated carbon surface. The interaction of two chlorine atoms with the active surface centres is conceivable. As depicted in Fig. 4, electron density may be transferred from the carbon surface towards lindane or an intermediate of the dehydrochlorination reaction. Technically, dechlorination of the hydrocarbon and chlorination of the carbon surface occur in this case.

In order to examine the contribution of this possible neutral reaction to the AC-mediated lindane hydrolysis, lindane was treated at initial pH values of 2.7 and 1.4 in the presence of AC. The initially applied pH value of 2.7 shifted slowly in the presence of AC due to its large buffer capacity. A pH value of 7.0 was finally reached at the 40th reaction day. Nevertheless, the reaction was followed for an additional 67 days during which the pH value remained

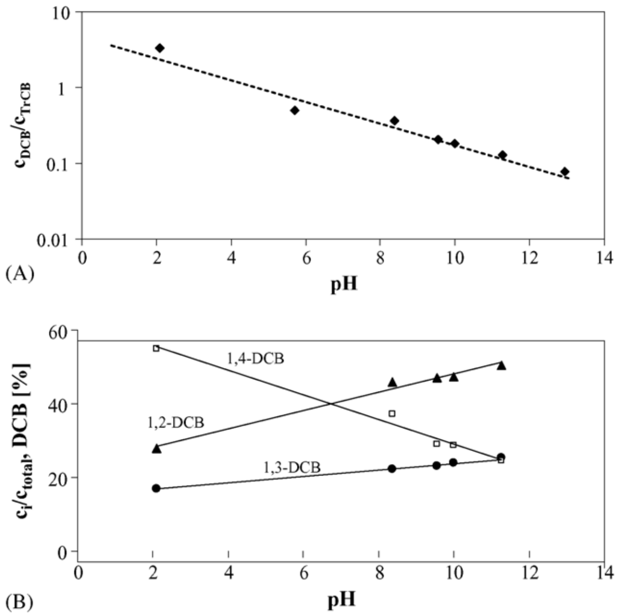

Fig. 3. (A) Product ratio $c_{DCB}/c_{TrCB}$ (concentration of dichlorobenzene isomers to concentration of trichlorobenzene isomers) at various pH values in the presence of 2 g $L^{-1}$ AC. (B) Distribution of dichlorobenzene isomers at various pH values.

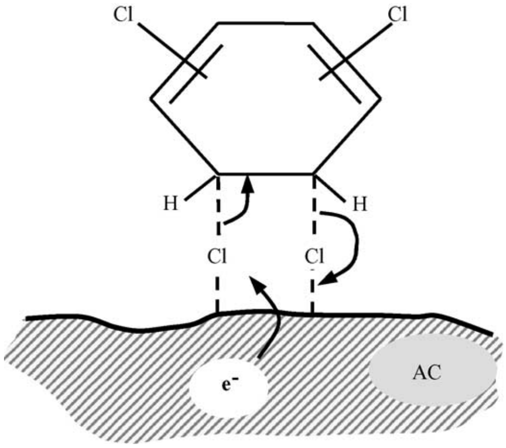

Fig. 4. Possible reaction mechanism for the formation of dichlorobenzene during lindane hydrolysis in the presence of activated carbon.

approximately constant at pH 7. We deliberately did not add any organic pH buffers which could have resulted in interference with the AC surface. During the second experiment, a pH shift from 1.4 to 2.2 was observed after a reaction time of 73 days. The dehydrochlorination of lindane to PCCHe was slow, as would be expected under acidic conditions. After 7 days 0.13%, 12 days 0.29%, 24 days 0.49%, 28 days 0.37% and after 73 days 0.7% of the introduced lindane was found to have been converted to PCCHe. These few data values allow a pseudo-first-order kinetics rate coefficient $k' \approx 1 \times 10^{-9}\ \mathrm{s}^{-1}$ to be estimated. However, the corresponding apparent second-order rate coefficient $k_b \approx 10^3\ \mathrm{L\,mol^{-1}\,s^{-1}}$ at a mean pH ≈ 2 would be about five orders of magnitude higher than that in homogeneous solution, which is very unlikely. Despite the very slow hydrolysis reaction in acidic suspension, the results indicate a significant neutral hydrolytic lindane cleavage without participation of hydroxide ions. This heterogeneous reaction can be formally described by first- or second-order rate coefficients $k' \approx 1 \times 10^{-9}\ \mathrm{s}^{-1}$ or $k_n = k'/c_{H_2O} \approx 2 \times 10^{-11}\ \mathrm{L\,mol^{-1}\,s^{-1}}$, respectively. Product analysis revealed only traces of DCB and TrCB beside the primary product PCCHe. As in the above reactions, the 1,2,4-isomer was the dominant TrCB, whereas among the DCB the *p*-isomer dominates (Fig. 3B). Evidently, the pH value influences the distribution pattern of DCB; this could be an indication for the competing reaction mechanisms (base-promoted and neutral hydrolysis). In acidic milieu, DCB are the preferred products compared to TrCB.

Approximately neutral aqueous solutions or suspensions (e.g. aquifers or surface waters) are those with the highest environmental relevance. The lindane conversion in neutral AC suspension follows a pseudo-first-order kinetics with $k' \approx 4.5 \times 10^{-6}\ \mathrm{s}^{-1}$ which leads to an apparent rate coefficient for the $OH^-$-mediated reaction at pH 7 of $k_b \approx 45\ \mathrm{L\,mol^{-1}\,s^{-1}}$ (Table 1). Under these conditions the TrCB:DCB ratio was about 1.2 ± 0.3. The heterogeneous reaction pathway leading to DCB (involving a 2-Cl-abstraction step) successfully competes with the conventional dehydrochlorination towards TrCB—the sole observed reaction mechanism in homogeneous solution.

Similar observations as described in the present paper with activated carbon have been published recently by Liu et al. [20] using mackinawite (amorphous FeS) as reductant. They also found dichlorobenzenes beside trichlorobenzenes from lindane in the presence of suspended FeS. They interpret their findings as a result of three types of reaction: (i) a neutral dehydrochlorination ($k' = 6.5 \times 10^{-9}\ \mathrm{s}^{-1}$ at 25 °C and pH ≤ 6.7), (ii) a base-mediated dehydrochlorination ($k_b \approx 0.04 \pm 0.01\ \mathrm{L\,mol^{-1}\,s^{-1}}$ at pH 8.3–12.0), and (iii) a heterogeneous reductive dichloro-elimination ($k_{FeS} = 1.3 \times 10^{-7}\ \mathrm{s}^{-1}$ at pH 6.9–8.3). The reductive dechlorination is a factor of 20 faster than the neutral dehydrochlorination at the applied experimental conditions (pH ≈ 6.8, 20 g $\mathrm{L^{-1}}$ FeS). If we compare the rate enhancing effects of FeS (5.2 mg $\mathrm{L^{-1}}$ lindane + 20 g $\mathrm{L^{-1}}$ FeS) with that of activated carbon (enhancement factor of $10^3$ with 100 mg $\mathrm{L^{-1}}$ lindane + 2 g $\mathrm{L^{-1}}$ AC) the much higher efficiency of activated carbon as reductant becomes evident. The difference amounts to about four orders of magnitude (in terms of rate enhancing factor times $c_{\mathrm{lindane}}/c_{\mathrm{reductant}}$). This may be at least partially due to the different surface areas of the two reductants (10 and 1000 $\mathrm{m^2\,g^{-1}}$ for FeS and AC, respectively). It may be instructive for elucidation of reaction mechanisms to compare the isomers distribution of the di- and trichlorobenzenes produced by the two different reductants. Liu et al. [20] found the following distribution of chlorobenzenes in the homogeneous alkaline hydrolysis at pH 12—1,2,4-TrCB:1,2,3-TrCB:1,3,5-TrCB = 50:30:20, which is qualitatively similar to our analyses (88:5:8). The principal composition of the TrCB fraction is equal in the homogeneous and in the two heterogeneous reaction systems, only slightly depending on the pH value. This indicates the same formation mechanism of TrCBs, a three step dehydrochlorination reaction. The DCB fraction possesses the following composition: 1,4-DCB:1,2-DCB:1,3-DCB ≈ 1:0.5:0 with FeS [20] and 1:1:0.5 (depending on the pH value, cf. Fig. 3B) with activated carbon as reductant. The most significant difference is the formation of 1,3-DCB with AC, which was not detected in the presence of FeS. This points to different surface mediated elimination mechanisms, as can be expected for such different reductants as FeS and activated carbon.

## 4. Conclusions

Compared to the alkaline hydrolysis of lindane in homogeneous solution, which has a rate coefficient of $k_b = 0.01–0.05\ \mathrm{L\,mol^{-1}\,s^{-1}}$ at pH ≥ 10 [1,6,7], the significant increase in the reaction rate in the presence of activated carbon is obvious. In addition to the formation of trichlorobenzenes, a novel reaction pathway leading to dichlorobenzenes was found in the presence of AC. The pH value controls the overall hydrolysis rate, the relative contributions of the homogeneous and heterogeneous reactions and the product distribution. Because the reaction pathway leading to DCB is only observed in the presence of AC, it can be concluded that the carbon surface acts not only as sorbent, but also as reaction partner. This also follows from the partial reduction of the carbon in the substrate, from $C^{\pm 0}$ in lindane to $C^{-1/3}$ in DCB.

Other saturated halogenated substances, such as 1,1,2,2-tetrachloroethane, 1,1,1,2-tetrachloroethane, 1,1,2-trichloethane and 3-bromopropanol were also found to be subject to an accelerated base-promoted hydrolysis in the presence of activated carbon compared to that in homogeneous solution [19]. In all cases, higher initial reaction rates were observed in the presence of activated carbon. Working with real groundwaters instead of model water, this catalytic effect could not be sustained for a long period of time (analogously to [13]), due to deactivation of the AC.

Nevertheless, the presented hydrolysis reactions open up possibilities for the advantageous utilization of AC in environmental processes not only as adsorber but also as catalyst, reaction partner and as a simple tool for increasing the retention time in fixed-bed reactors. In the case of fixed-bed reactors, the gross turnover or reactor performance is a function of the residence time of the substrates in the reaction zone, i.e. the available reaction time. The residence time is approximately proportional to the distribution coefficient $K_d$ (for $K_d \gg 1$). Therefore, a hydrophobic compound has a very long residence time in an AC fixed bed reactor, which greatly benefits the reactor performance, provided that the sorbed substrate is still available for the chemical, possibly catalytic reaction. Even this has been demonstrated in the present study for the hydrolysis of lindane, which can be considered as a model reaction between a hydrophobic substrate and hydrophilic reactants ($OH^-$ and $H_2O$).

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