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# Hydrodehalogenation of halogenated hydrocarbons in water with Pd catalysts: Reaction rates and surface competition

Katrin Mackenzie *, Heike Frenzel, Frank-Dieter Kopinke

*Department of Environmental Technology in the Centre for Environmental Research Leipzig-Halle, D-04318 Leipzig, Germany*

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**Abstract**

Hydrodehalogenation using Pd catalysts has proved to be an efficient reaction for water detoxification. In the present study, reaction rates for a variety of halogenated hydrocarbons with hydrogen as reductant in aqueous catalyst suspensions have been measured. Structure–reactivity considerations allow the prediction of reactivities of various halogenated organic compounds in water clean-up processes. The correlation of C–Cl bond strength with the hydrodechlorination rate earlier reported was reassessed. In contrast to straightforward structure–reactivity correlations found for chloroalkanes, hydrodehalogenation rates of chloroethenes and halobenzenes do not follow the order of the C–X bond strength. Here, the addition of an activated hydrogen species from the catalyst to the unsaturated hydrocarbon seems to be the rate-determining step.

For pollutant mixtures, hydrodehalogenation rates were influenced by competition for Pd surface sites. Competitors diminish reaction rates depending on their sorption strength towards the Pd surface. Substances subject to extremely slow hydrodehalogenation (such as methylene chloride and fluorobenzene) showed no marked influence on other competitors. The heavier halogens, bromine and iodine (whether as R–X or as $X^-$), dominate all competing effects. However, no self-poisoning of the catalyst for hydrodehalogenation of iodo- and bromohydrocarbons occurred in the water phase. This makes it possible to reduce these halogenated compounds at reasonable rates over Pd catalysts.

Under optimal conditions, the activity of Pd catalysts is so high that external and intraparticle mass transfer limitations cannot be ruled out for hydrodehalogenation of many substrates in aqueous catalyst suspensions.

*Keywords:* Catalytic hydrodehalogenation; Palladium catalysts; Structure–reactivity relationship; Surface competition

## 1. Introduction

Halogenated organic compounds (HOCs) are among the most widely distributed and prevalent pollutants in wastewaters and contaminated groundwaters. These contaminations have encouraged a great deal of effort towards finding efficient treatment methods other than stripping and adsorption. Methods which destroy the halogenated substances under moderate conditions, with minimal energy input, are particularly sought-after. Hydrodehalogenation of water pollutants using palladium catalysts has been widely studied over the last decade and is one of the most promising methods for detoxification of organohalogen waste and pollutants [1,2]. Palladium catalysts have proved to be well suited for promoting hydrodehalogenation reactions in the gas phase as well as in the aqueous phase following the equation $C_lH_mX_n + nH_2 \rightarrow C_lH_{m+n} + nHX$ [3,4]. In the course of the reaction, olefinic double bonds are hydrogenated whereas aromatic units are usually preserved.

Most papers dealing with Pd-catalyzed hydrodehalogenation are devoted to gas-phase reactions. Often reactions are carried out in solvents or solvent–water mixtures under conditions inappropriate for environmental applications. Reaction mechanisms and deactivation tendencies in water can be substantially different from hydrodehalogenation in other media such as the gas phase or a mixed liquid phase. Compared to the number of papers concerning gas phase reactions and reactions in solvent mixtures, markedly fewer authors deal with hydrodehalogenation in the water phase (e.g. [5–18]). However, a few working groups do describe the field application of Pd catalysts for hydrodehalogenation in ground- or wastewater (e.g. [19–25]).

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* Corresponding author.

*E-mail address:* katrin.mackenzie@ufz.de (K. Mackenzie).

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Although many groups are working on hydrodehalogenation, the data provided generally concern the reaction of single substances under specific conditions with a variety of catalysts. A systematic comparison of reported substrate reactivities and catalyst selectivities is difficult. It is known, for instance, that the ease of the hydrolytic cleavage of C–X bonds depends upon several parameters, such as the type of the halogen X (Cl, Br, I) attached to the organic skeleton [1]. Catalyst poisoning due to halogenide ions released during the reaction is often counteracted by carrying out the reaction in the presence of a base [1,26]. The mechanism of the base effect is not clear, and increased pH values are not generally applicable in practice for environmental catalysis. Stronger catalyst poisons, such as sulphide ions, can deactivate the catalyst in the water phase irreversibly [19,27]. Various hydrogen sources have been tested as replacements for molecular hydrogen in order to overcome the limited $H_2$ solubility in water [1,28]. There is concurrent evidence that besides structural features of the substances [29–33] also the composition of the reaction media [26,34,35], certain reaction products [1,35,36], the nature of the catalyst support [35], competitive reactions of other compounds [37,38] and the particle size of the catalyst [39–42] can all strongly influence the reaction rates in hydrodehalogenation reactions. In order to predict contaminant degradation time frames and selectivities in fixed-bed reactors or treatment zones under environmental conditions, the influencing parameters must be known.

The objective of this work is the comparison of first-order rate coefficients for the Pd-catalyzed hydrodehalogenation of a variety of halogenated hydrocarbons, depending on the compound structure and pollution composition.

## 2. Experimental

All reagents and HOCs were purchased in the highest grade available from Merck (Germany) or Sigma–Aldrich (Germany) and used as received. The catalyst used was G-133D Pd on $\gamma$-$Al_2O_3$ egg-shell catalyst in pellet form with 0.5 wt% Pd, the catalyst has a BET surface area of about 160 $m^2\,g^{-1}$ and has been purchased from Commercia (Germany). The granular catalyst was crushed and sieved. The fraction 63–125 $\mu$m was applied in the batch experiments. The Pd content of the sieved fraction was 0.52 wt% (determined by EDXRF analysis). This catalyst will be referred to as Pd/$Al_2O_3$. Prior to use, the catalyst samples were pre-reduced with $H_2$ in aqueous suspension for 1 h.

The hydrodehalogenation studies were carried out as batch experiments. Amber screw-cap bottles (250 ml) equipped with Mininert® valves were used. The 200 ml reaction solution (typically 1 mM HCl to provide constant chloride background and constant pH value during the course of the dehalogenation experiments) was extensively purged with $H_2$ prior to adding the aqueous catalyst suspension (10–100 mg catalyst, corresponding to a Pd input of 0.25–2.5 mg $L^{-1}$) and the HOC as methanolic solution. The catalyst concentration was adjusted to the reaction rates in such a way that a sufficient number of samples could be analysed over the course of the reaction. The headspace over the suspension (50 mL) was pure $H_2$, yielding a sufficient reservoir of reductant. Typically, the HOCs were added first to the $H_2$-saturated reaction solution and brought to phase equilibrium. The reaction was started by adding the pre-reduced catalyst suspension (2 mL) by syringe, carefully excluding air. The bottle was then continuously shaken (180 rpm) throughout the experiment. The reaction kinetics was monitored by means of headspace analyses of educts and products using a GC–MS device (QP 2010, Shimadzu Corp., equipped with a DB1 capillary column). In addition, the reaction product halogenide was analyzed using an ion chromatograph (IC25, Dionex, equipped with an IonPac® AS15/AG15 column set). The experimental set-up chosen is based upon the following conditions: (i) the proportion of HOCs present in the headspace is small compared to that in the water phase ($K_{\mathrm{Henry}}V_{\mathrm{headspace}}/V_{\mathrm{water}} \ll 1$), (ii) the $H_2$ demand for complete hydrodehalogenation is small compared to the total hydrogen amount present in the reactor bottle (dissolved + headspace) and (iii) the mass transfer between aqueous and gas phase is fast compared to the reaction rates.

## 3. Results and discussion

When choosing catalytic hydrodehalogenation as a means for detoxification of contaminated water, one should bear in mind that literature data obtained from gas-phase studies (at elevated temperatures) or experiments in solvent mixtures might diverge from what is to be expected in pure water at ambient or groundwater temperature. Hoke et al. found, e.g. a lower sensibility of Pd catalysts for chloride poisoning when water is added to the reaction system in organic solvents [26], which shows that the affinity of chloride ions towards the protic solvent water helps to withdraw the reaction product from the Pd surface.

Within the present study, the reaction rates of a variety of HOCs with different structural features were investigated using a commercial Pd catalyst under well-defined reaction conditions in aqueous suspension. In order to provide a general tool for assessing the performance of various catalytic systems, the Pd-based specific catalyst activity $A_{\mathrm{Pd},i}$ was introduced. Hydrodehalogenation reactions of single compounds and HOC mixtures, where the compounds compete for reactive catalyst sites, were evaluated. In many cases, the hydrodehalogenation reaction follows a first-order kinetics with respect to the HOC concentration. The specific catalyst activity $A_{\mathrm{Pd},i}$ for the dehalogenation of the compound $i$ is calculated according to Eq. (1) [23]:

$$A_{\mathrm{Pd}}\,(\mathrm{L\,g^{-1}\,min^{-1}}) = \frac{V_{\mathrm{water}}}{m_{\mathrm{Pd}}\tau_{1/2}} = \frac{\ln(c_{t1}/c_{t2})}{\ln 2\, c_{\mathrm{Pd}}(t_2 - t_1)} \qquad (1)$$

with $V_{\mathrm{water}}$ as the water volume applied, $m_{\mathrm{Pd}}$ and $c_{\mathrm{Pd}}$ as the Pd mass and concentration and $\tau_{1/2}$ as the HOC's half-life, obtained from its disappearance kinetics. $t_1$ and $t_2$ are two arbitrarily chosen sampling times and $c_{t1}$ and $c_{t2}$ are the

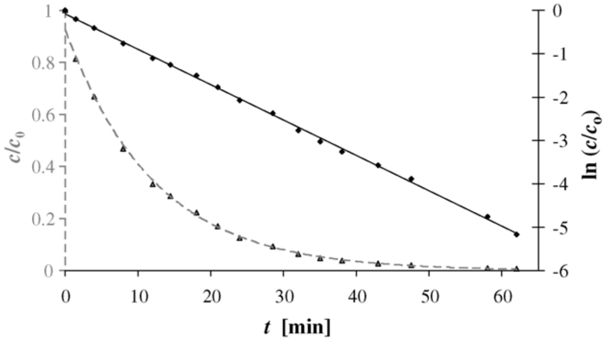

Fig. 1. Hydrodechlorination of chlorobenzene ($c_0 = 20$ mg $L^{-1}$) in an aqueous $Pd/Al_2O_3$ suspension ($c_{catalyst} = 30$ mg $L^{-1}$).

corresponding HOC concentrations. The catalyst activities were calculated either from the HOC conversion or from the product formation rates. The second approach was preferably used for low degrees of conversion. The value of $A_{Pd,i}$ is equivalent to a first-order rate coefficient $k_{obs}$ [$s^{-1}$] for the disappearance of the HOC $i$ according to $k_{obs} = \ln 2A_{Pd,i}c_{Pd}$. In order to obtain clearly interpretable kinetic data, saturation of the catalyst surface and mass transfer limitations were avoided as far as possible. Fig. 1 shows a typical concentration–time curve over a broad conversion range ($\leq 99\%$).

Apparently, the reaction follows a first-order kinetics. However, apparent first-order kinetics of a heterogeneous reaction does not prove that the observed rate coefficient actually reflects the chemical reaction step. It is well known from the chemical reaction engineering theory that external and intraparticle mass transfer limitations tend to shift the apparent reaction order towards one [43,44]. This aspect will be considered later on in the paper.

There is not a great deal to be found in the literature about mechanistic studies of hydrodehalogenation reactions. Moreover, the authors dealing with this topic refer exclusively to gas-phase reactions (e.g. [30,33,45]). The transferability to hydrodehalogenation in the water phase is not yet clear. However, similarities can be expected. Comparing the hydrodechlorination rates of saturated, olefinic and aromatic HOCs, we have to state that in contrast to iron as reducing agent, all three substance classes are in principle subject to dehalogenation using Pd catalysts. However, the catalytic reaction is highly substance-structure sensitive. Considering only chlorinated hydrocarbons, their relative reaction rates cover a range of more than 7 orders of magnitude (cf. Table 1). In our experience, at least three factors influence the hydrodehalogenation rate at the Pd surface in pure water: (i) the ease of bond scission depending on the C–X bond strength and, therefore, on the type and number of functional groups, (ii) the adsorption of the compound at the Pd surface and (iii) the presence or absence of a double bond close to the halogen substituent, which controls the prevailing reaction mechanism. The bond strength between halogen and the active metal is thought to be another key factor in controlling the reaction rates [46,47].

Table 1 shows values of C–X bond strength (as bond dissociation enthalpy) for a number of halogenated hydrocarbons, as well as the specific Pd activity which was experimentally determined from the hydrodehalogenation of each single compound (average of two or three replicates, $\leq 20\%$ deviation between parallel runs). The reactivity grading regarding chloromethanes and chloroethanes strictly follows the ease of C–Cl bond scission. Tetrachloromethane is dechlorinated quickly—more than 12 times faster than chloroform.

Table 1
Specific Pd activities $A_{Pd,i}$ in the hydrodehalogenation reaction of single substances and C–X bond strengths $D_{C-X}$ ($c_{cat} = 10$–$100$ mg $L^{-1}$ $Pd/Al_2O_3$, 1 mM HCl, $c_{0,HOC} = 1$–$10$ mg $L^{-1}$)

| Substance | | $D_{C-X}$ [kJ $mol^{-1}$] | $A_{Pd,i}$ [L $g^{-1}$ $min^{-1}$] |
|---|---|---|---|
| Tetrachloromethane | $CCl_4$ | 306[a] | 10 |
| Chloroform | $CHCl_3$ | 339[a] | 0.8 |
| Methylene chloride | $CH_2Cl_2$ | 350[a] | $1.5 \times 10^{-3}$ |
| 1,1,1,2-Tetrachloroethane | $C_2H_2Cl_4$ | 295[c] | 100 |
| 1,1,1-Trichloroethane | $C_2H_3Cl_3$ | 309[c] | 15 |
| 1,1,2,2-Tetrachloroethane | $C_2H_2Cl_4$ | 314[c] | 3 |
| 1,2-Dichloroethane | $C_2H_4Cl_2$ | 348[c] | $3 \times 10^{-4}$ |
| *cis*-1,2-Dichloroethene | $C_2H_2Cl_2$ | 370[b] | 670 |
| *trans*-1,2-Dichloroethene | $C_2H_2Cl_2$ | 373[b] | 670 |
| Tetrachloroethene | $C_2Cl_4$ | 382[b] | 210 |
| Trichloroethene | $C_2HCl_3$ | 392[b] | 420 |
| 1,1-Dichloroethene | $C_2H_2Cl_2$ | 394[b] | 850 |
| Vinyl chloride | $C_2H_3Cl$ | 452[c] | 1180 |
| Iodobenzene | $C_6H_5I$ | 274[a] | 450 |
| Bromobenzene | $C_6H_5Br$ | 337[a] | 380 |
| Chlorobenzene | $C_6H_5Cl$ | 399[a] | 200 |
| Fluorobenzene | $C_6H_5F$ | 524[a] | $3 \times 10^{-3}$ |

[a] Ref. [48].
[b] Ref. [47].
[c] Ref. [49].

Where different C–X bonds are present, $D_{C-X}$ refers to the weakest C–X bond in the molecule.

Methylene chloride has until now been considered as recalcitrant in the Pd-catalyzed hydrodechlorination in water at ambient temperature. However, following the very slow methane evolution for several weeks allowed us to estimate a rate coefficient for the methylene chloride hydrodechlorination. The shaken reaction vessel was kept inside a nitrogen-purged water vessel during the extended reaction time in order to minimize gas leakage and air penetration into the system (competing reaction at the active Pd sites: $0.5O_2 + H_2 \rightarrow H_2O$).

Methyl chloride as a product of partial dechlorination of methylene chloride was detected in traces (about 0.2 mol% of methane). Likewise, the other chlorinated methanes form predominantly methane in a single step. The release of partially chlorinated intermediates was small ($< 5\%$) under all conditions, but may be significant with respect to the overall treatment result. $CHCl_3$ reacts 12 times more slowly than $CCl_4$. If a ‘complete’ reduction of HOCs is necessary, the reaction conditions have to be adjusted in such a way that even the less reactive intermediates are degraded [23]. This can dramatically increase the required reactor performance necessary for achieving the goal.

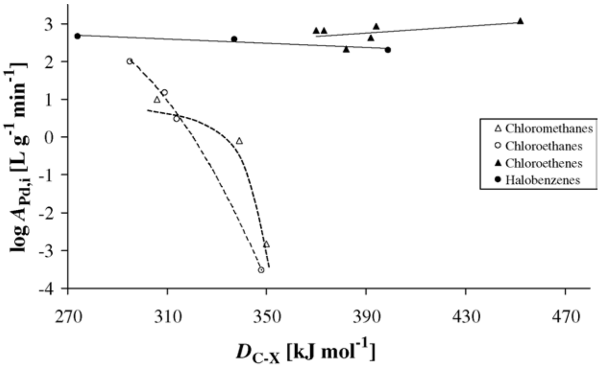

Fig. 2. Correlation of hydrodehalogenation rates with C–X bond strengths of chlorinated alkanes, ethenes and monohalogenated benzenes (data from Table 1).

In addition to partial hydrodehalogenation, hydrogenation of unsaturated compounds may be an undesired side reaction at Pd catalysts. Kopinke et al. [23] found hydrogenation of vinyl chloride to ethyl chloride to be the dominant reaction at 50 °C in the gas phase. Fortunately, in the aqueous phase the elimination of halogenide is much faster than the hydrogenation of double bonds. Otherwise, the whole concept of Pd-catalyzed hydrodehalogenation would collapse, because hydrogenation results in stabilization of the halogenated target compounds.

The specific Pd activity towards chloroethanes imparts roughly the same impression as given by chloromethane hydrodechlorination: the reaction rate strongly correlates with the C–Cl bond strength (cf. Fig. 2). The number of geminal Cl atoms in the molecule is more important than their total number. This may, e.g. be explained by (i) the weakening of C–Cl bonds by further geminal Cl substituents and (ii) the better initial steric attachment of several Cl atoms to the Pd centres.

Both the affinity to the Pd surface and the C–Cl bond strength may influence the hydrodechlorination rate. Chen [33] predicted an inverse correlation between C–Cl bond strength and the heat of adsorption of chlorinated compounds from the gas phase on the Pd surface. In this way, both processes – adsorption and irreversible bond scission – were driven by the same molecular property. The dissociative adsorption of chlorinated compounds was postulated as the rate-determining step. Several authors predicted the formation of carbene-like structures on the Pd surface as intermediates of hydrodehalogenation reactions in the gas phase (e.g. [46,50]). However, for dehalogenation in the water phase at ambient temperature this seems less likely. Other authors report homolytic cleavage on the Pd surface for aliphatic structures [33,51,52]. Evidence for a slightly different mechanism with chlorobenzene as a representative of aromatic hydrocarbons has been described by Coq et al. [3].

In contrast to the straightforward structure–reactivity correlation found with chloroalkanes, hydrodechlorination rates of olefins do not follow the order of the C–Cl bond strength. For example, vinyl chloride – the compound with the strongest C–Cl bond – is dechlorinated fastest. The hydrodechlorination rate is inversely correlated with the number of Cl atoms at the double bond. However, the graduation between the various ethenes is relatively small: a factor of 6 between vinyl chloride and tetrachloroethene. Obviously, the hydrodechlorination mechanism for olefins is different from that for saturated chlorohydrocarbons. A plausible hypothesis to explain our findings is the addition of a H atom from the Pd surface to the double bond as the rate-determining reaction step. The C–Cl bond is broken later at the reaction coordinate. The adverse impact of Cl substituents on the reaction rate may be attributed to their electron-withdrawing effect, which weakens the Pd–olefin-π-complex (adsorption step) or lowers the reactivity of the double bond for an electrophilic H addition (reaction step).

The halogenated benzenes are approximately as reactive as the chlorinated ethenes. Apparently, the large differences in the strength of C–Cl, C–Br and C–I bonds do not play a significant role. This is again a strong indication that the rate-determining step for hydrodehalogenation of unsaturated substrates is not the C–X scission, but more likely the transfer of a hydrogen species from the catalyst surface to the substrate molecule.

In a recent review by Tratnyek et al. [53], quantitative structure–activity relationships (QSAR) for chemical reduction reactions are discussed, including the reductive dechlorination with zero-valent iron. Nothing is known from this review about Pd-catalyzed reactions. In contrast to our findings with $H_2$/Pd as reductant, the $Fe^0$-driven dechlorination yields similar correlations for chlorinated alkanes and alkenes. This indicates a common reaction mechanism for the two HOC classes, which is most likely based on an electron transfer from iron to the HOC in the rate-determining step. Unfortunately, $Fe^0$ is not able to reduce chlorinated aromatics.

It is very seldom that groundwater pollutions are single-compound contaminations. Usually, several pollutants occur as mixture. Therefore, it is essential to know the possible interferences when working with substance mixtures. Table 2 shows the influence of competitor HOCs on the specific Pd activity of selected halogen compounds.

On the one hand, those substances with the highest affinity to the Pd surface, as is apparent for iodohydrocarbons and trichloroethene, remain almost unaffected by the presence of competitor reactants. On the other hand, substrates with the lowest reactivity, such as methylene chloride and fluorobenzene, do not significantly affect reaction rates of other competitors. In a mixture of six chloroethenes ($c_0$ = 1 mg L$^{-1}$ each) all the rate coefficients were similarly diminished by a factor of 1.6 ± 0.2 compared to those from single-substance experiments. The lower the ratio of the rate coefficients $k_{obs,single}$/$k_{obs,mixture}$ in Table 2 is, the stronger the HOCs are adsorbed on the Pd surface. Apparently, the π-electron system of chlorobenzene has no advantage over aliphatic chlorocompounds. Summarizing the data in Table 2: competition effects between various chlorocompounds are significant but not huge (less than a factor of 6). They are much more pronounced for bromo- and iodobenzene which clearly out-compete the chlorocompounds.

First-order reaction kinetics and competitive effects are two findings which do not simply match the same mechanistic picture. We explain this with the interaction of reaction kinetics

Table 2
Rate coefficients in the hydrodehalogenation under competitive conditions (HOC mixtures) in comparison to single-substance rate coefficients ($c_{cat}$ = 10–100 mg L$^{-1}$ Pd/Al$_2$O$_3$, 1 mM HCl)

| Mixture | $c_{0,i}$ [mg L$^{-1}$] | $\frac{k_{obs,single}}{k_{obs,mixture}}$ |
|---|---|---|
| Tetrachloroethene | 1 | 1.6 |
| Trichloroethene | 1 | 1.6 |
| 1,1-Dichloroethene | 1 | 1.8 |
| *cis*-1,2-Dichloroethene | 1 | 1.4 |
| *trans*-1,2-Dichloroethene | 1 | 1.4 |
| Vinyl chloride | 1 | 1.4 |
| Trichloroethene | 2 | 2.8 |
| Chlorobenzene | 2 | 5.7 |
| 1,1,1,2-Tetrachloroethane | 2 | 2 |
| Trichloroethene | 2 | 1.3 |
| Chlorobenzene | 2 | 3.3 |
| Chlorobenzene | 2 | ≥100 |
| Bromobenzene | 2 | 1.1 |
| Trichloroethene | 10 | 1 |
| Methylene chloride | 10 | n.a. |
| Trichloroethene | 10 | 1.9 |
| Toluene | 10 | Not reactive |
| Fluorobenzene | 50 | n.a. |
| Chlorobenzene | 50 | ≥100 |
| Bromobenzene | 50 | 95 |
| Iodobenzene | 50 | 1.3 |
| Fluorobenzene | 50 | n.a. |
| Chlorobenzene | 50 | 1.1 |
| Iodobenzene | 50 | 1.1 |
| Tetrachloromethane | 50 | 70 |
| Chlorobenzene | 10 | 2.5 |
| Tetrachloromethane | 10 | 1.2 |

n.a., not analysed.

and mass transfer effects, which tend to converge towards an overall apparent first-order kinetics (see below).

In principle, HOCs can compete for reactive catalyst sites *or* for reactive hydrogen species. This question can be decided by application of a non-reactive but sorption-active competitor such as toluene. Toluene does not react (by hydrogenation) under the applied conditions. Hence, it does not compete for hydrogen species. Nevertheless, it inhibits hydrodechlorination of trichloroethene by a factor of about 1.8 (Fig. 3). This is a clear indication of competition for catalyst sites rather than for hydrogen species.

Halogenide ions are also potential competitors for surface sites. As the desired reaction product they are unavoidable under all reaction conditions. Although Pd is considered to be the hydrodehalogenation catalyst which is least affected by chloride ions [1,54], halogenide ions may still have a substantial affinity towards Pd [55] even in aqueous solution [56].

Not only the halogen species released during the reaction at the catalyst surface but also freely-dissolved halogenide ions may compete with the HOCs for Pd surface sites. In order to simulate the salinity of natural waters and to provide a near-constant bulk-phase chloride concentration during the course of the reactions, all reaction solutions contained a 1 mM chloride 'plinth' (addition of HCl or NaCl). Fig. 4 shows the hydrodechlorination of two HOCs – chlorobenzene and trichloroethene – when bromide ions (50 mg L$^{-1}$) were added. Bromide clearly slowed down the reaction of both HOCs by a factor of about 3. Like toluene, bromide is a non-reactive competitor which competes for Pd-surface sites.

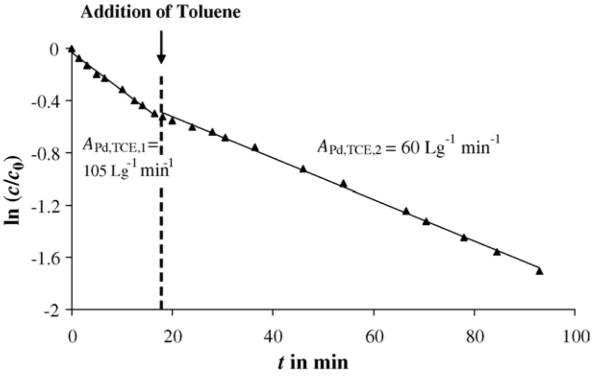

Fig. 3. Effect of toluene addition on the hydrodechlorination rate of trichloroethene ($c_{TCE,0}$ = 10 mg L$^{-1}$ each, $c_{catalyst}$ = 15.5 mg L$^{-1}$, 1 mM HCl, $c_{toluene}$ = 50 mg L$^{-1}$).

Lower bromide concentrations (5, 10 and 20 mg L$^{-1}$) caused only marginal changes in the observed dechlorination rates. Surprisingly, even in the presence of 500 mg L$^{-1}$ bromide the hydrodechlorination of trichloroethene still proceeds at an appreciable rate (about 1/5 of the rate with pure TCE). It is possible that bromide does not compete for all types of active sites.

The data in Table 2 indicate that the heavier halogens determine the course of the reaction for contaminant mixtures. This effect is known from solvent–water mixtures under elevated pressure and temperature [32]. The affinity of bromide and especially iodide ions to the Pd surface is apparent from the described suppression of chlorobenzene reactivity. Iodide ions added were found to have this effect on other pollutants, independent of the substance class. Surprisingly, we did not find a self-poisoning in hydrodeiodation reactions. The iodide ions formed inhibited hydrodechlorination and debromination; however, substances such as iodobenzene, iodobutane, iodo-

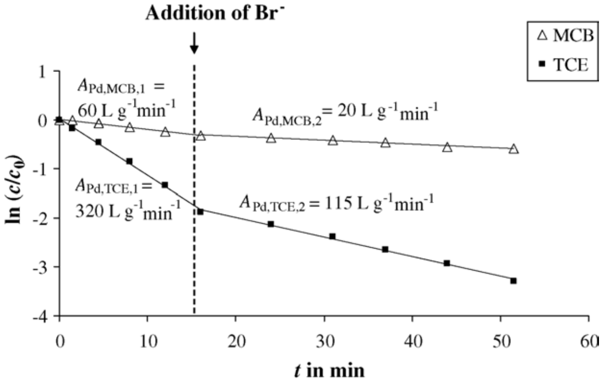

Fig. 4. Effect of bromide addition on the hydrodechlorination rates of chlorobenzene (MCB) and trichloroethene (TCE); $c_{HOC,0}$ = 2 mg L$^{-1}$ each, $c_{catalyst}$ = 10 mg L$^{-1}$, 1 mM HCl, $c_{Br^-}$ = 50 mg L$^{-1}$.

methane, triiodobenzoic acid and iodoanisol are rapidly and completely reduced using Pd catalysts. For iodobenzene and iodoanisol, multiple reaction cycles did not lead to catalyst breakdown. The iodohydrocarbons seem to compete successfully with the released iodide ions for the Pd surface sites. However, when iodocompounds are present, the Pd function for hydrodehalogenation of chloro- and bromocompounds is poisoned.

As we have demonstrated, Pd on $\gamma$-$Al_2O_3$ is a powerful catalyst for hydrodehalogenation in aqueous suspension at ambient conditions. The highest catalyst activity was measured for vinyl chloride with $A_{Pd} = 1180\ L\ g^{-1}\ min^{-1}$. This value corresponds to a half-life of about one minute for vinyl chloride in the presence of 1 mg Pd per litre water to be treated. On the one hand, highly active catalysts are desirable. On the other hand, they make it very difficult or even impossible to measure the 'true' reaction kinetics. We are aware of the fact that the reaction rates measured in this study are affected by mass transfer limitation—the higher the rates, the more dominant this limitation is. Approximating an *external* mass transfer coefficient in the order of $k_L \approx 3 \times 10^{-4}\ m\ s^{-1}$ [57] in the agitated batch reactor, the external transport resistance can be estimated as about 50% for $A_{Pd} = 250\ L\ g^{-1}\ min^{-1}$. Higher catalyst activities are even more affected. In order to obtain an estimate of the *intraparticle* transport resistance we calculated the dimensionless Weisz-modulus $\Phi$ [43,44] for the reaction of vinyl chloride under the applied conditions:

$$\Phi = L_C^2 \frac{k_{eff}}{D_{eff}} = \left(\frac{10^{-2}\ cm}{6}\right)^2 \frac{70\ s^{-1}}{(2 \times 10^{-6}\ cm^2\ s^{-1})} \approx 100 \tag{2}$$

with $L_C$ as a characteristic length which characterizes the diffusion distance inside the catalyst particle. For spherical particles it is equal to 1/6 of the particle diameter ($d_{particle} \approx 100\ \mu m$). $k_{eff}$ is the first order rate constant of the substrate reduction related to the catalyst volume: $k_{eff} = \ln 2 \times A_{Pd} c_{Pd\ in\ catalyst} = 0.7 \times 1180\ (L\ g^{-1}\ min^{-1}) \times 0.005\ (g\ Pd\ (g\ catalyst)^{-1}) \approx 70\ s^{-1}$. The effective diffusion coefficient of halogenated hydrocarbons (R–X) inside the $\gamma$-$Al_2O_3$ particle was approximated as 1/10 of its value in water: $D_{eff,R\text{–}X} \approx 0.1 \times D_{R\text{–}X,water} \approx 2 \times 10^{-6}\ cm^2\ s^{-1}$. The resulting value of the Weisz-modulus $\Phi \approx 100$ indicates that the substrate inside the pore volume is strongly depleted compared with its bulk-phase concentration ($c_{pore,i}/c_{bulk,i} \approx 0.01$) [43,44]. To overcome intraparticle mass transfer resistance for such fast reactions we had to apply colloidal catalysts ($d \leq 1\ \mu m$). This, however, was not the intention of the present study dealing with particulate catalysts. What are the consequences of the mass transfer limitation? The apparent reaction order ($n_{obs}$) and rate coefficient ($k_{obs}$) are given by Eqs. (3) and (4).

$$n_{obs} = 0.5(1 + n_{reaction}) \tag{3}$$

$$k_{obs} = \left(k_{reaction} \frac{D_{eff}}{L_C^2}\right)^{0.5} \tag{4}$$

The measured reaction rates underestimate the "true" chemically-controlled rate coefficients. The scale of rate coefficients is compressed ($k_{obs} \sim k_{reaction}^{0.5}$). This may explain the curvature of the log $A_{Pd}$ versus $D_{C\text{–}X}$ correlation for chloroalkanes in Fig. 2. However, the qualitative pattern of rate coefficients is not affected, provided that the effective diffusivities of the various substrates are similar. Therefore, the mechanistic conclusions regarding the different chemical steps in hydrodehalogenation of saturated and unsaturated hydrocarbons remain valid.

## 4. Conclusions

Palladium-catalyzed hydrodehalogenation reactions in aqueous suspension are substance–structure sensitive. Within substance families of chloroalkanes, a direct dependence of the reaction rate on the C–Cl bond strength was observed. Estimation of reaction rates (or specific Pd activities) from C–Cl bond strength is in principle possible. In contrast to alkanes, in hydrodehalogenation of unsaturated compounds – olefins and aromatics – C–X bond strength is not the key property. We propose the addition of an activated hydrogen species from the catalyst to the double bond as the rate-determining reaction step. The adsorption strength of the halogenated compound on the Pd surface is another key parameter, which dominates the competition between different substrates.

Hydrodehalogenation of pollutant mixtures revealed pronounced competition effects for Pd surface sites in the 10–100 μM concentration range. The affinity of iodo- and bromocompounds to palladium is very high and dominates all competing effects. Hydrodechorination is strongly inhibited in the presence of brominated and iodocompounds. The halogenide ions released also compete for the Pd surface. However, a self-poisoning of iodo- and bromohydrocarbons was not observed.

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