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# Considerations on the mechanism of Ca/ethanol/Pd/C assisted hydrodechlorination of chlorinated aromatic substrates

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## HIGHLIGHTS

- Ca assisted hydrodechlorination is an effective decontamination procedure.
- Zeta potential experiments demonstrate that reaction occurs in the vicinity of the catalyst.
- Involvement of molecular hydrogen was set aside.
- Hydrodechlorination mechanism is probably radicalic.

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## ABSTRACT

In order to elucidate the metal-alcohol hydrodechlorination reaction mechanism, several experiments using chloroanisoles as substrates were performed. Thus, chloroanisoles were stirred at 60 °C for 2 h with a mixture of Ca, methanol and various reduction catalysts. The use of deuterated methanol and zeta potential experiments offered supplementary informations, pointing toward a probable radicalic mechanism that occurs on Ca and Pd/C surfaces.

## 1. Introduction

The investigation of hydrodechlorination processes represents an important aspect for the chemists working in the field of environmental remediation, since the high toxicity of persistent organic pollutants (POPs) such as ubiquitous polychlorinated aromatic compounds (*e.g.* dioxins and PCBs) has been demonstrated (Birnbaum, 1994). Thus, various approaches were developed, ranging from thermal, chemical or photochemical forms of activation (Haglund, 2007) to newer methodologies such as biological, radiolytic or mechanochemical (Kulkarni et al., 2008). Compared to those methods, reductive dechlorination (*a.k.a.* hydrodechlorination) proved to be advantageous in terms of energy consumption and remediation efficiency (Wu et al., 2012), needing only a mixture of a metal and a hydrogen donor (Keane, 2011; Ghaffar and Tabata, 2010; Mudhoo et al., 2013). For example, Chen and coworkers were one of the many using zero-valent iron for the decontamination of PCBs polluted soils (Chen et al., 2014). On the other hand, Wang et al. preferred the combination of Fe with Pd for the hydrodechlorination of dioxins (Wang et al., 2010a,b), while other researchers chose bimetallic systems consisting of iron

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with nickel or lead (Zhu et al., 2011, 2012; Nie et al., 2013).

For their part, Bokare or Kim used zero-valent zinc for the reductive dechlorination of octachlorodibenzo-*p*-dioxin (Bokare et al., 2013; Kim and Carraway, 2003), while Sun switched from Zn to Cu (Sun et al., 2013). Other metals tested for their hydrodechlorinating capacities were Ni, with or without Pd (Wang et al., 2010b; Amorim et al., 2011), or in combination with another metal such as Cu (Yin et al., 2012). In our case, the choice metal was Ca for its safety in handling, environmental innocuity and commercial availability (Mitoma et al., 2001, 2004, 2006a,b, 2009a,b, 2011; Simion et al., 2012).

Almost all of the previous studies dealt with the scope and limitations of the reported processes, as well as their applications to the decontamination of various matrixes (water, soil, fly ash etc.). However, a small number of these studies presented reaction mechanism data, mostly in the form of reaction pathways (Atkinson et al., 2015). More consideration has been given to the mechanism of catalytic hydrodechlorination (Yakovlev et al., 2000; Sajiki et al., 2002). Nevertheless, in those specific papers that treated the problem of the reaction mechanism (not only from a kinetic point of view), the catalyst surface is usually considered to be the only reactive site (Zhou et al., 2010). The influence of the proton donor and pH was also investigated, showing that slightly acidic conditions are favorable to the hydrodechlorination process (Kopinke et al., 2004). Some studies suggested up to three different mechanisms, implying hydrogen species of different nature: radical, hydride, or a hydride-like radical (DeVor et al., 2009). We have been studying the hydrodechlorination of aromatic halides for more than a decade, introducing our system formed of metallic Ca and an alcohol as hydrogen donor, making some contributions to the mechanistic study of this process (Mitoma et al., 2009b). Since other research teams were inclined to use a similar system (a metal and an alcohol) (Maloney et al., 2011), we decided to scrutinize more carefully the mechanistic implications of the hydrodechlorination process involving a metal and an alcohol and to compare our results with those presented in the literature.

### 1.1. Experimental part

Commercially available alcohols (Wako Pure Chemical Industries Ltd.) and distilled water were used, Granular particles of metallic calcium were purchased from Kishida Chemical Co. Ltd. (99%, particle size distribution: 2–2.5 mm, surface area: 0.43–0.48 $m^2$/g). The 5% Rh/C, Pd/C, Ru/C, Pt/C and Re/C were acquired from Aldrich Chemical Co. (particle size distribution: 3.0–271 μm, average of distribution: 40–50 μm, surface area: 500–600 $m^2$/g, BET). Calcium and reduction catalyst were used with no pre-treatment. Chlorinated anisoles (>99.0%, GC) were purchased from Aldrich Chemical Co. Sealed and pressure resistant tubes of 35 mL volume from Ace Glass, Inc. were used. For some experiments, we used a portable reactor (38 mL internal volume TVS-1 type from Taiatsu Techno Corp.), which permitted the measurement of the variations of the internal pressure, respectively of the temperature, with a pressure gauge and a thermocouple thermometer. On a typical procedure all components were loaded into the reaction tubes; the reaction mixture was magnetically stirred and kept at the right temperature for the duration of the experiment.

### 1.2. Hydrodechlorination process

As a general experimental procedure, 1 mmol substrate was introduced in a pressure glass reaction tube, provided with thermal and pressure sensors, along with 4 mmol metallic Ca, 0.1 g of a reduction catalyst and 5 mL of alcohol or water. The reaction mixture was stirred at various temperatures (25 °C, 40 °C, 60 °C, 70 °C) for 2 h reaction time and next quenched in aqueous HCl. After 2 h, 20 mL of 1 M nitric acid was added and the reaction mixture was subsequently extracted four times using 100 mL diethyl ether (both acid treatment were necessary to eliminate all traces of any metal). Combined organic layers were washed, dried on $MgSO_4$ and evaporated. The crude reaction mixtures were subjected to GC and GC-MS analyses. The GC-MS analyses were conducted using a gas chromatograph (HP 6890 series) equipped with a 30 m of DB-5 ms column (i.d. 0.25 mm) (J&W Scientific Inc.) and a quadrupole mass spectrometer (JMSAM II series; JEOL). Ionization was performed under 70 eV electron-impact conditions. Assignment of structures was performed through a search of the GC-MS library. Another gas chromatograph (30 m DB-1 and FID detection, GC-2010; Shimadzu Corp.), provided with a recorder (C-R6A Chromatopac; Shimadzu Corp.) was used for routine work and yield determination. Both GC programs were identical: the initial temperature of the column was 40 °C, for the first 3 min; then the temperature was first increased with a rate of 15 °C/min up to 150 °C and next with 40 °C/min up to 250 °C, where the temperature was maintained for 4 min.

The experiments with deuterated alcohols were conducted using the same protocol, the sole difference being replacing usual $CH_3OH$ with either $CD_3OH$ or $CH_3OD$.

### 1.3. Catalytic hydrogenation experiments

2-Chloroanisole (2.1 mmol or 1 mmol), methanol (10.5 mL or 5 mL, respectively) and reduction catalyst (0.21 g or 0.1 g) were introduced in a stainless steel hydrogenation reactor. The established $H_2$ pressure was maintained for 2 h, at a temperature of 60 °C. The final work-up of the reaction mixture proceeded as described above, followed by a GC-MS analysis.

### 1.4. Zeta (ζ) potential measurements

All ζ potential were determined using a ZEECOM ZC-2000 zeta potential analyzer (Microtec, Chiba, Japan) by taking the average of (at least) five measurements at stationary level. Dry methanol was introduced into a H-type cell (model T1205; 6 mL volume, width and thickness being of 10.0 mm, respectively 0.76 mm), equipped with Pt electrodes (9.0 cm distance between). The viscosity and permittivity of the methanol solution were of 0.0059 Poise, respectively 33 F/m. The electrodes chambers were separated by a squared, transparent, cell of 0.15 mm (in the front) to 0.61 mm (in the back). The position for observation and measurement was 0.15 mm from the cell's surface. The temperature was kept at a constant 25 °C and the voltage at 25.0 V. Each measurement's duration was of exactly 4 s. The ZEECOM ZC-2000 zeta potential analyzer uses microscopic electrophoresis for the identification of particles through automatic tracking in image processing. All investigated mixtures were prepared separately; samples were taken by micropipette and introduced in the H-type cell. Initially, the substrate consisting of C or Pd/C was cleansed, dried and suspended in methanol, and ζ potential was measured for these mixtures. Next, various amounts of Ca were added to either only C or to Pd/C substrates. After a strong stirring at 300 rpm, each mixture was allowed to rest for 10 min. A constant volume from the upper suspension was collected witha micropipette and submitted to ζ potential determination, the values being directly given.

## 2. Results and discussion

As main objective of this mechanistic study, the hydrodechlorination of *o*-, *m*- and *p*-chloroanisoles **1a-c**, as parent