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Mechanistic Considerations on the Hydrodechlorination Process of Polychloroarenes

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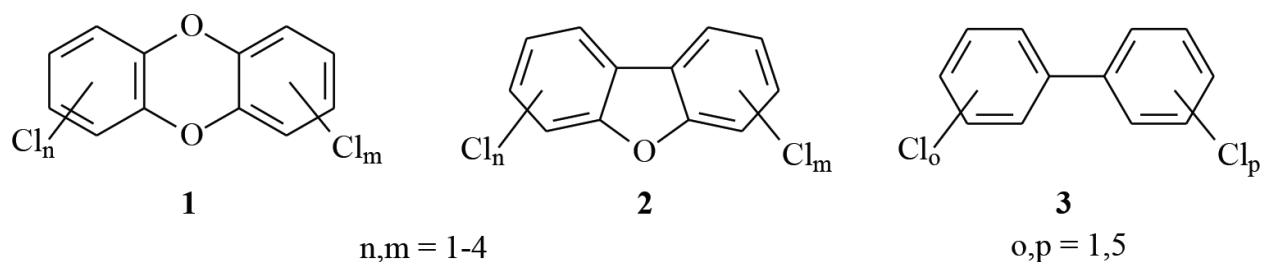
Abstract

Defunctionalization of organochlorines through reductive dechlorination (also known as hydrodechlorination—replacement of chlorine atoms by hydrogen—is one of the main methodologies used in the detoxification of these harmful compounds. Most of the published papers on this particular matter focused on specific reagents, reaction conditions, and mainly result efficiency. Some of the authors were also concerned with reaction pathways (e.g., the order in which chlorine atoms were removed from a polychlorinated aromatic substrate—polychlorinated biphenyls, PCBs; polychlorinated dibenzo-*p*-dioxins, PCDDs; or polychlorinated dibenzofurans, PCDFs). However, the papers that dealt with the investigation of reaction mechanism were rather scarce. This chapter presents the advances made by researchers in understanding, from a mechanistic point of view, the hydrodechlorination process, along with our own assumptions. In doing so, it would be easier to predict the behavior of such compounds in a specific environment, showing more clearly the scope and limitations of each process, depending on the reaction conditions and reagents.

Keywords: hydrodechlorination, reaction mechanism, metal/hydrogen donor

1. Introduction

Most chlorinated and especially polychlorinated arenes (such as polychloro-dibenzo-*p*-dioxins **1**, polychloro-dibenzofurans **2**, or polychlorobiphenyls **3**) are persistent organic pollutants (POPs) that are harmful to both man and the environment [1–5].



As a result, numerous techniques and procedures were implemented for their destruction/degradation [6–11]. Initially, these procedures focused on the separation/extraction of polychlorinated compounds and subsequent treatment. Nowadays, researchers value the in situ procedures the most, with the advantage of time and the economic aspects [7, 12–14]. Indeed, such compounds are stable molecules, which are resistant to hydrolysis, oxidation, and temperature changes, thus being difficult to degrade and showing long half-life times in the environment [15]. For example, dioxins could have atmospheric half-lives of 10–20 years, while, in soils, they can reach staggering values of up to 150 years.

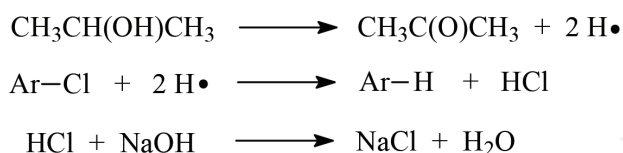
This means that it might be an impossible task to deliver a dioxin-free Earth for future generations, but it lies on the present generation of scientists and engineers to try to do so. In that spirit, early attempts appealed to mankind's most powerful discovery of destructive technology—fire [16]. In the early 1990s, most of the processes were thermal. But as it was soon discovered, these procedures were in fact a source for a *de novo* polychlorinated compound synthesis, the process by which dioxins are re-formed being investigated in the recent years [17–19]. Therefore, greater attention was focused on more chemical-based processes [6, 10, 20–23], along with microbial ones [24].

In particular, attention was focused on those procedures that were based on the combination of a metal and a hydrogen donor, processes that allowed the hydrodechlorination of the polychlorinated aromatic substrate to less toxic hydrocarbons [6–9, 14, 21–23]. Since these are among the most studied procedures in the past few years, we turned our attention to the particular reaction mechanism of the hydrodechlorination reaction. Indeed, understanding the reaction mechanism of a particular process is important in view of understanding the role played by each reagent but also in view of the predictive modeling of similar processes or the same process applied to various other substrates [25].

2. Proposed hydrodechlorination mechanisms—Literature survey

From an historical perspective, the formation of polychlorinated arenes (PCDDs, PCDFs, and PCBs) were first investigated [23, 26–34] and soon the catalytic role of various metals was understood [35–41]. If metals can do, they can also undo: indeed, they can effectively intervene in numerous defunctionalization processes, including hydrodechlorination [22, 42]. Since the process implies a reductive approach, researchers naturally oriented themselves toward reduction catalysts, such as Ru, Rh, Pd, or Pt. One remark must be made for the pioneering efforts of Ukisu and coworkers [43–46], who used a hydrogen donor (isopropanol),

NaOH, and Pd/C or Ru/C. Ukisu also provided the first insights on the possible reaction mechanism of the hydrodechlorination process, apprehending the intervention of atomic (or nascent) hydrogen:



Later on, Ukisu also tried to explain the intervention of the catalyst. Based on much earlier studies, Ukisu stated that the dehydrogenation of 2-propanol to acetone on rhodium complexes implied the elimination of a hydride ion [47]—Ukisu assumed that the α -hydrogen of isopropanol transfers to PCDD/F in the form of hydride, on the catalyst's surface [45, 46], the reaction resembling to an aromatic nucleophilic substitution (**Figure 1**):

The trail of reduction catalysts is still a heavily investigated one. Ayame's team started from the premise that, in the catalytic hydrodechlorination of monochlorobenzene, the hydride ion formed on the Pd surface spills over the alumina carrier surface and attacks the electron-deficient carbon of a monochlorobenzene adsorbed on Lewis acid sites of the alumina to produce a benzene molecule and a chloride ion. The chloride ion, which coordinated to a Lewis acid site, would be converted to hydrogen chloride in the reaction with H^+ spilled over from the Pd surface [48]. However, most scientists were at that point more interested in the various pathways with regard to the reactivity of the differently positioned chlorine atoms [49–54]. Based on density functional theory calculations, rules of thumb for assessing the reductive dechlorination pathways of PCDDs were proposed [55]. These included “(1) the chlorine atoms in the longitudinal (1,4,6,9) positions are removed in preference to the chlorine atoms on lateral (2,3,7,8) positions; (2) the chlorine atom that has more neighboring chlorine atoms at ortho-, meta- and para-positions is to be eliminated; (3) reductive dechlorination prefers to take place on the benzene ring having more chlorine substitutions; and (4) a chlorine atom on the side of the longitudinal symmetry axis containing more chlorine atoms is preferentially eliminated” [55].

Anyway, one important aspect resulted from these studies, and that is, that adsorption phenomenon on the catalyst's surface certainly play a role in the process [49, 56, 57]. Nevertheless, there was no consensus on the hydride transfer mechanism. If such transfer seems plausible when an alcohol is used as hydrogen donor [43–46, 54], and even if the formation of hydride

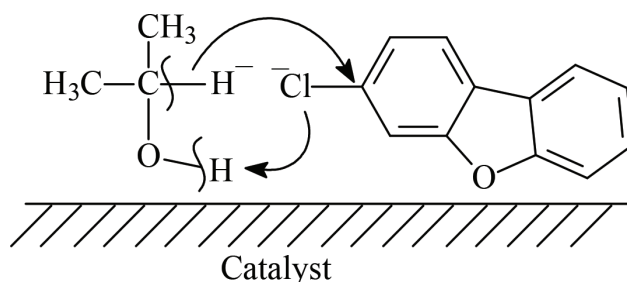


Figure 1. Ukisu's hydrodechlorination mechanism proposal [45, 46].

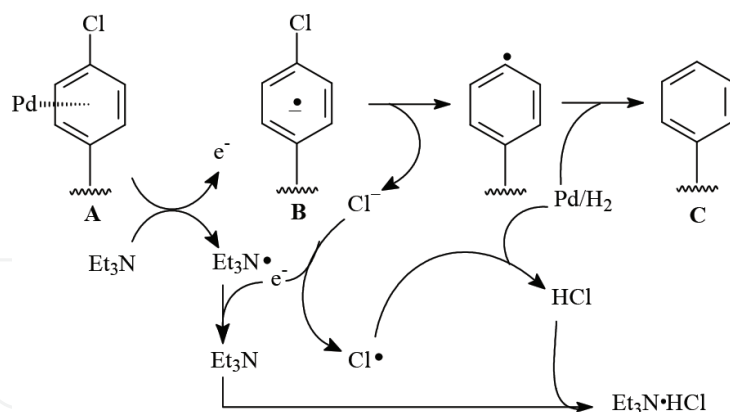
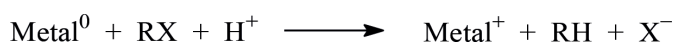


Figure 2. Tentative mechanism of the hydrodechlorination of aromatic chlorides [58].

is postulated when molecular hydrogen is involved (through a heterolytic dissociation of H_2) [48], for Hirota and coworkers, the reaction mechanism involves a single-electron transfer (SET) step [58]. This team used triethylamine (instead of NaOH) for HCl trapping, its role being also an activator of the Pd/C-catalyzed hydrodechlorination process. Upon addition to the hydrodechlorination reaction mixture of small amounts of tetracyanoethylene or 7,7,8,8-tetracyanoquinodimethane, which are well-known electron scavengers, the reaction was suppressed, suggesting thus a single-electron transfer (SET) mechanism (**Figure 2**).

The SET mechanism was reprised in several other papers in which the reaction conditions were more suitable for such a process: either photochemical [59, 60] or electrochemical [61]. The radicalic mechanism was also the center of hydrodechlorination processes, involving more active metals such as Na or K [62, 63], the main argument being the recorded formation of compounds such as quarterphenyls (as results of Fittig-Wurtz-type coupling). Another testimony for the single-electron transfer mechanism came from the study of a dual depolluting process for industrial wastewaters simultaneously polluted with chlorinated compounds and nitrites/nitrates. The authors observed a competition for electrons between reductive dechlorination and denitrification— NO_3^- is reduced to NH_4^+ retarding the dechlorination due to the competition for electrons [64].

Nevertheless, the use of metals in the palette of hydrodechlorination processes took a new turn with used metals such as iron, zinc, magnesium, or calcium [65, 66]. Again, for these techniques, the electron transfer from the metal, with subsequent formation of nascent hydrogen through reaction with a proton donor prevailed, the process being summarized as:



Among the metals tested, iron occupies a place of choice, used either alone [66–68] or in combination with other metals, especially Pd or Pt [57, 66, 69–74]. Three mechanisms were proposed to explain the observed dechlorination process [66]: one that involves direct electron transfer from Fe to the adsorbed alkyl halide ($Fe^0 + \text{RX} + \text{H}^+ \rightarrow Fe^{2+} + \text{RH} + \text{X}^-$) and other two that involve corrosion of Fe in water under anaerobic conditions ($Fe^0 + 2H_2O^+ \rightarrow Fe^{2+} + H_2 + 2OH^-$). The idea of using a bimetallic system, Pd along with Fe, made the process much more effective (**Figure 3**):

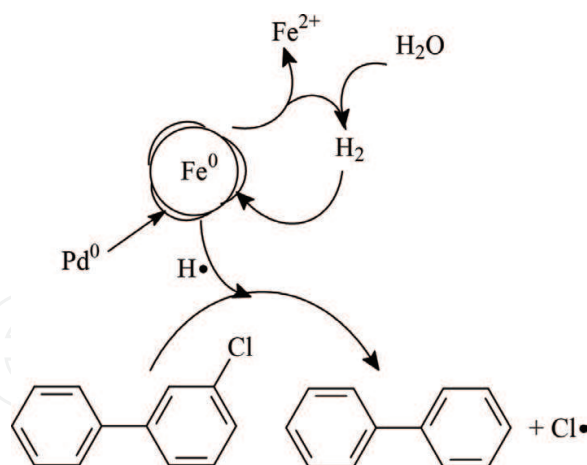


Figure 3. Proposed surface reaction of PCBs with Fe/Pd nanoparticles [74].

An interesting twist to the method is represented by the replacement of Fe with Mg in Fe/Pd [75–78], which is based on the following reasons: Mg has a relatively high oxidation potential (2.37 V; Fe has just 0.44 V), providing thus a greater thermodynamic force, and, while Fe tends to rather rapidly corrode, Mg can form a protective magnesium oxide shell (**Figure 4**).

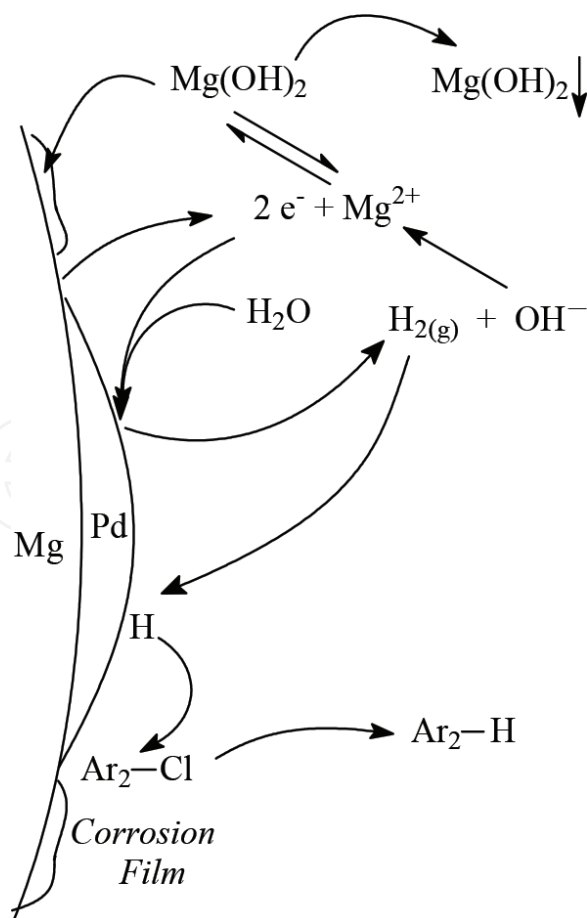


Figure 4. Proposed mechanism for the dechlorination of PCBs over Mg/Pd [76].

A comparison of the hydrodechlorination effectiveness of Pd-deposited metals (Mg, Al, Mn, Zn, Fe, Sn, and Cu) was made by Yang et al. [79], who found that, in acidic aqueous solution, Mg/Pd present the highest reactivity, while at the other end are Sn and Cu that showed little to none dechlorination capability.

An important breakthrough in understanding the reaction mechanism of palladized magnesium-mediated hydrodechlorination was made by the Geiger team [80–83]. By working in pure methanol, the source of H_2 is the reaction between Mg and the alcohol ($Mg^0 + 2CH_3OH \rightarrow Mg(CH_3O)_2 + H_2$). The reaction exhibits pseudo-first-order kinetics, and the order of dechlorination rates of chlorine atoms in 100% methanol is ortho->para->meta-positions, which differ from that in water/methanol (9:1 v/v) or 100% water (para->meta->ortho-). But, more importantly, the possible reaction mechanisms were discussed. This team proposed either an $S_{RN}1$ mechanism or an $S_{RN}1$ type of mechanism, in which a nucleophilic substitution, involving a radical intermediate, occurs. One major difference from classical $S_{RN}1$ mechanism though is that the initiation step is the homolytic rupture of the C-Cl bond by either atomic hydrogen or hydride ion, with subsequent formation of aryl radical and HCl. In the more classical $S_{RN}1$ mechanism, an aryl radical anion is formed due to hydride formed on bulk Pd. Basically, the three proposed mechanisms differ by the nature of the hydrogen involved: simple radicalic H (or atomic/nascent H), atomic H with an enhanced negative charge (a radical-anion H with a fractional negative charge – $H^{\bullet-}$), or a hydride ion (H^-) (Figure 5).

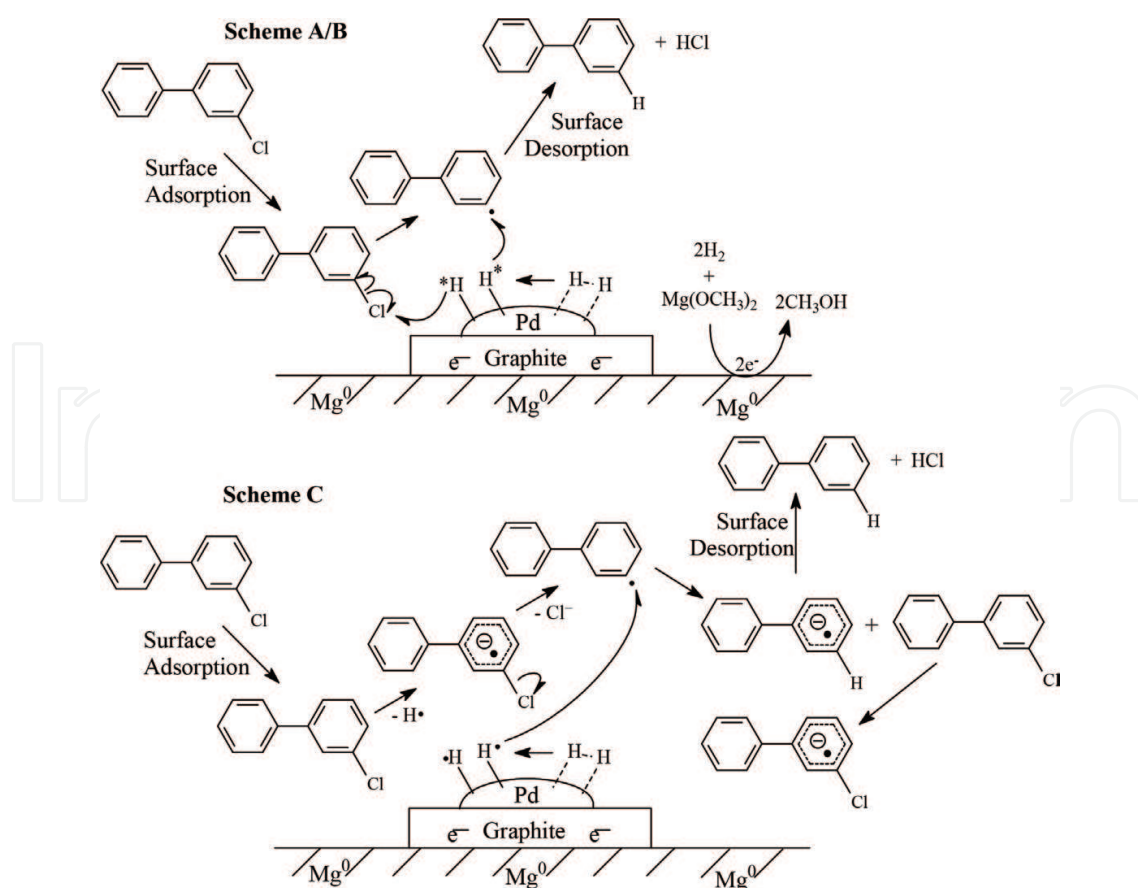


Figure 5. Proposed mechanism for the dechlorination of PCBs by Mg/Pd in methanol by scheme A/B atomic hydrogen or “hydride-like” radicals, and scheme C hydride (H^- denotes both hydrogen and “hydride-like” species) [82].

An interesting assumption for the hydride mechanism is that the latter act as a nucleophile, which can transfer an electron to the aromatic chlorinated substrate, which will cause the elimination of a chlorine atom, leaving an aryl radical. This aromatic radical can quickly react with another H^\bullet . The charged biphenyl species can then transfer an electron to another PCB substrate, so that process can continue to propagate.

Among the reasons given for the possibility that all three mechanisms could occur are the fact that both atomic hydrogen and hydride species can be formed on Pd from molecular hydrogen and the lack of dimerization products (quarterphenyls) or additional chlorinated by-products. These mechanisms require initial adsorption of the PCBs onto the surface of the bimetallic system, then reaction at the interface of the palladium and graphite, limiting thus considerably the mobility of the aryl radical. This limited mobility and the abundance of atomic hydrogen, hydride-like radicals, and hydrides on the surface of the catalyst almost certainly allow for the reaction of the aryl radical and second nucleophilic hydrogen rather than two separate aryl radicals coming into contact [82].

For similar reasons, Ca was used instead of Mg [84–91]: not only does Ca have an even higher thermodynamic driving force when compared to Fe or Mg (0.44 V—Fe, 2.37—Mg, 2.87—Ca) but also CaCO_3 coating both protect metallic Ca surface and is easily removed, allowing this procedure to be applied both ex situ and in situ (**Figure 6**).

Two potential mechanisms were proposed over the years: one purely radicalic, that involves nascent hydrogen, and one radicalic but which implies a pseudo-nucleophilic substitution mechanism in which the addition of electrons from calcium ($\text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{e}^-$) transforms the aromatic ring into a radical-anion that rapidly expels chlorine atoms. The hydrogen atom on the hydroxyl group of the alcohol is then added to the radical anion yielding a hydrodechlorinated substrate and an alkoxide (**Figure 7**).

Upon working with deuterated methanol (CH_3OD), the authors observed both the formation of deuterodechlorination products and aryl dimers, suggesting the intermediacy of the radicalic aryl species [84].

Recent results based on zeta potential determinations and hydrodechlorination reactor's internal pressure monitorization suggested that the radicalic process could be favored. Indeed, no pressure rise is a hint that molecular H_2 is not formed in the reaction $\text{Ca}^0 + 2\text{CH}_3\text{OH} \rightarrow \text{Ca}(\text{CH}_3\text{O})_2 + \text{H}_2$

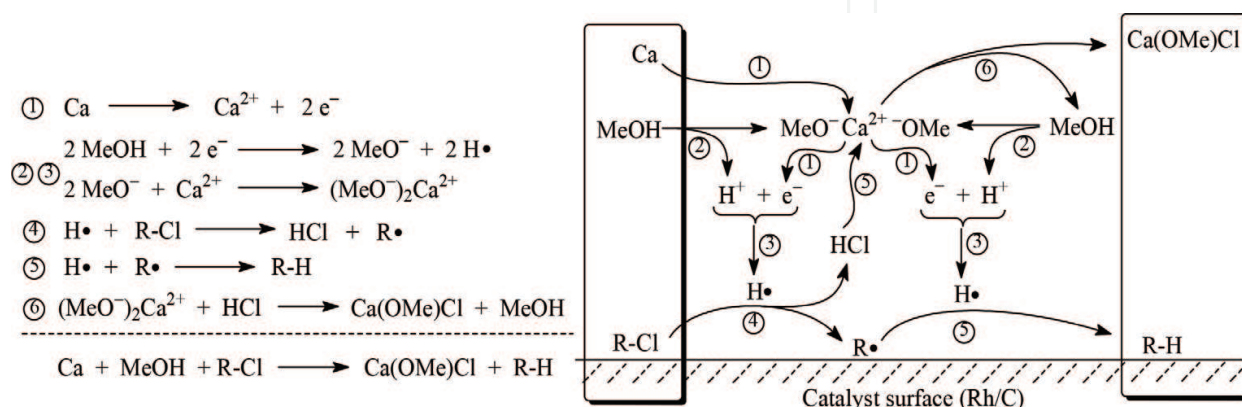


Figure 6. Possible dechlorination pathway [88].

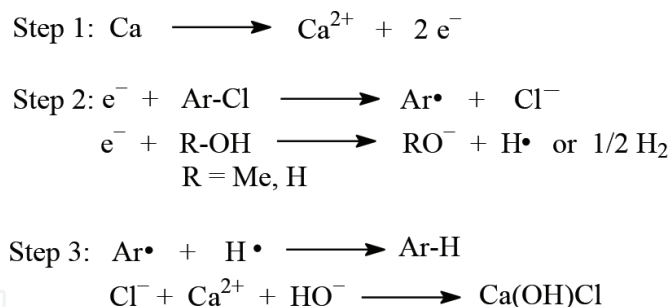


Figure 7. Hydrodechlorination mechanism following a pseudo-nucleophilic aromatic substitution [87].

but instead nascent hydrogen is generated: $\text{Ca}^0 + 2\text{CH}_3\text{OH} \rightarrow \text{Ca}(\text{CH}_3\text{O})_2 + 2[\text{H}]$. Thus, the authors assumed that during the hydrodechlorination process of chloroanisole, the only proton source is the alcoholic (protic) hydrogen, the mechanism being most probably radicalic (the recorded formation of biphenyls as coupling products is an indication for this). Even at lower H_2 pressures, the hydrodechlorination of chloroanisole to anisole was achieved in at least 95% or even higher yields. The reaction efficiency implies that the transfer of atomic hydrogen (formed in calcium reaction with methanol) to catalyst surface (such as Pd/C) proceeded directly, without the formation of molecular hydrogen in solution. The surface of the catalyst showed differential conditions electrostatically, depending on the concentration of calcium as electron source (Figure 8).

Along with metallic Ca, other Ca compounds were tested in a hydrodechlorination process: Ca(OH)_2 [92], CaO [93–95] or CaSiO_3 [95]. Although most of these studies favored a radicalic mechanism, Gao and coworkers [95] discussed alternative pathways that involved either an electron transfer (with subsequent formation of a radical-anion that expels the chlorine anion and form the aryl radical) or a direct hydrogen transfer (in an $\text{S}_{\text{RN}}1$ -type mechanism). Based on calculations of the adiabatic electron affinities of PCDFs, the chloride ion dissociation yielding aryl radicals is considered the major pathway of chlorine abstraction [96]. Moreover, when traces of Cu are present, Ullman-type coupling products can be formed.

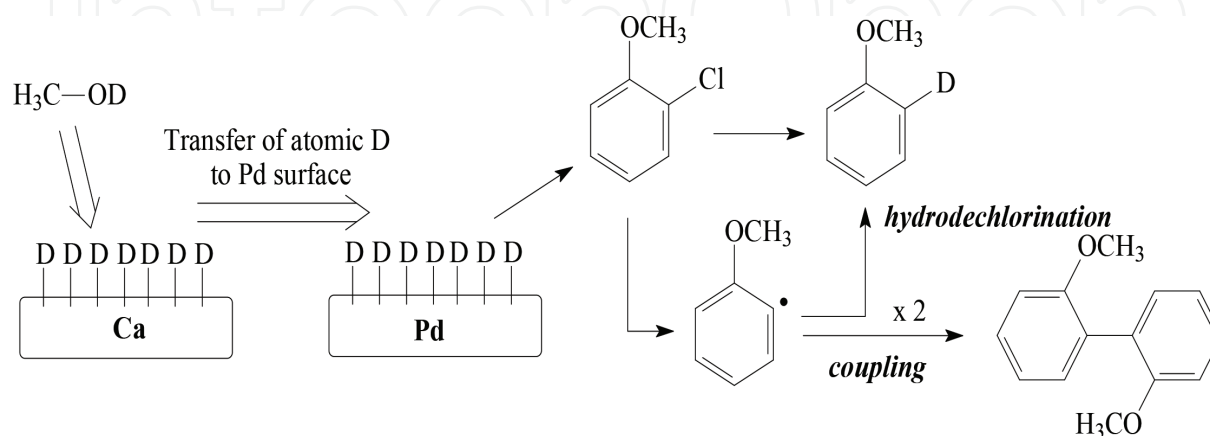


Figure 8. Proposed reaction pathway and deuterium route from $\text{H}_3\text{C-OD}$ to deuterodechlorination product [84].

Similar mechanistic observations were made by different teams that used metals other than Fe, Mg, or Ca. For example, for a zero-valent Zn hydrodechlorination of tetrachlorophenol, the intermediate in the reaction mechanism is again the aryl radical formed by expelling the chlorine anion from the initial radical-anion [97]. The latter is considered to be formed by the aromatic ring quenching of an electron from zero-valent Zn ($1/2\text{Zn}^0 \rightarrow 1/2\text{Zn}^{2+} + 1\text{e}^-$) (Figure 9).

Analogous conclusions were drawn for bimetallic systems such as Fe/Ni [98], Mg/Zn [99], or Ni/Mo [100].

Another approach was taken by Lim and coworkers when comparing the performances of Pd/Fe nanoparticles with other bimetallic systems such as Pt/Fe, Ni/Fe, Cu/Fe, and Co/Fe nanoparticles during the hydrodechlorination of trichlorophenol [72], since the process was studied in an aqueous environment. Starting from the premise that chlorinated organic compound treatment in water were reduced according to three different mechanisms—(1) direct reduction on fresh zero-valent iron (ZVI) surface, (2) reduction by ferrous iron, and (3) reduction by H_2 through catalysis [101]—the authors assumed that the bimetal/water system, having a stronger reductive ability, allowed more easily the formation of an activated reducing species, atomic hydrogen (H^*) (Figure 10).

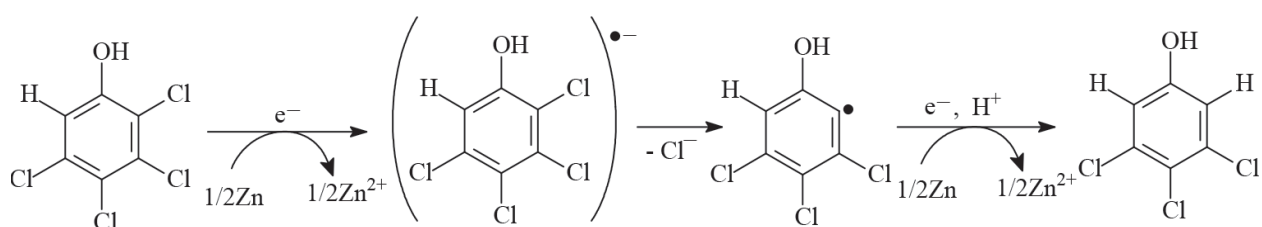


Figure 9. Hydrodechlorination of tetrachlorophenol with zero-valent Zn [97].

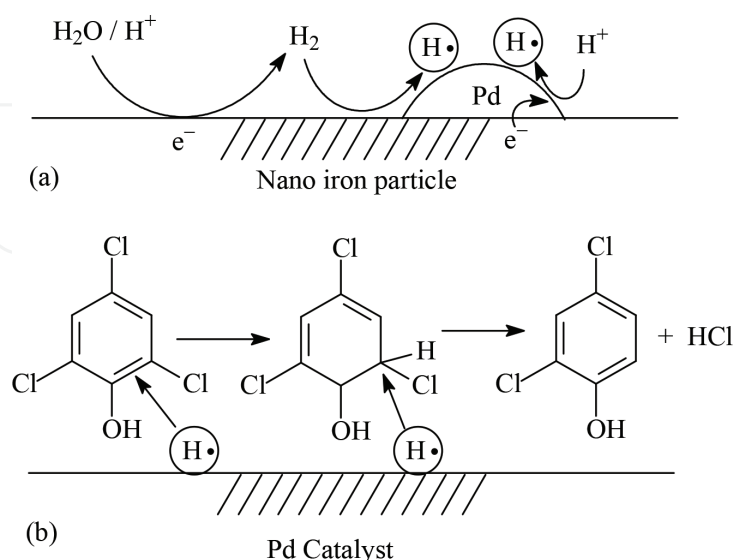


Figure 10. Schematic of proposed catalytic hydrodechlorination mechanism of chlorophenols over nanoscale Pd/Fe (a) production of atomic hydrogen and (b) surface-mediated hydrodechlorination of chlorophenols on Pd surface [72].

The production of H^* may follow two routes: catalyzed decomposition of H_2 gas to H^* and electron abstraction by H^+ . For this particular process, the authors considered more plausible electrophilic addition, followed by subsequent elimination of HCl through a dehydrodechlorination process.

But when considering that the degradation process occurs in water or even in supercritical water, true aromatic nucleophilic substitution of the chlorine atoms (and their replacement by $-OH$ moieties) could be considered [102, 103]. In just supercritical water and under oxidative conditions, the hydroxylated PCB only accounted for less than 10% of the reaction mass, while for alkaline, non-oxidative conditions the formation of hydroxylated PCBs could nearly close the mass balance in the early stage of PCB degradation [102]. The authors concluded that the formation of comparable amounts of PCDFs (requiring two oxygen substitution steps under preservation of both aromatic systems) in the experiments under oxidative and non-oxidative, alkaline conditions indicated that under both treatments, an oxygen substitution under preservation of the aromatic rings is the major initial step. On the other hand, hydroxylated PCBs are less susceptible to nucleophilic substitution compared to PCBs due to the electron-donating effect of the $-OH$ group. Therefore, under the alkaline, non-oxidative conditions, the initial degradation products (hydroxylated PCBs) are less reactive toward further degradation compared to the starting compounds (PCBs). But when the treatment occurs in the presence of Co_3O_4 , the reaction pathway, involving the formation of chlorophenolate and dichlorophenolate, is similar to the Mars Van Krevelen mechanism [104]. Nucleophilic substitution of the chlorine atom occurs through attack of the lattice oxygen atoms (O^{2-}) and a $Co-Cl$ bond is formed, yielding chlorophenolate and dichlorophenolate as partial oxidation products. Similar reaction routes have been reported for the formation of phenolates during the degradation of HCB over Al_2O_3 [105] and the degradation of chlorobenzene over iron and titanium oxide catalysts [106] (**Figure 11**).

An even more suggestive hint of a nucleophilic substitution of chlorine atoms was represented for the catalytic degradation of PCBs with Ni complexes [107]. A simplified model of the successive reactions was presented, clearly suggesting in steps 3 and 4 a nucleophilic attack of a hydride ion upon the aromatic chlorinated substrate:

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1. Ligand displacement:

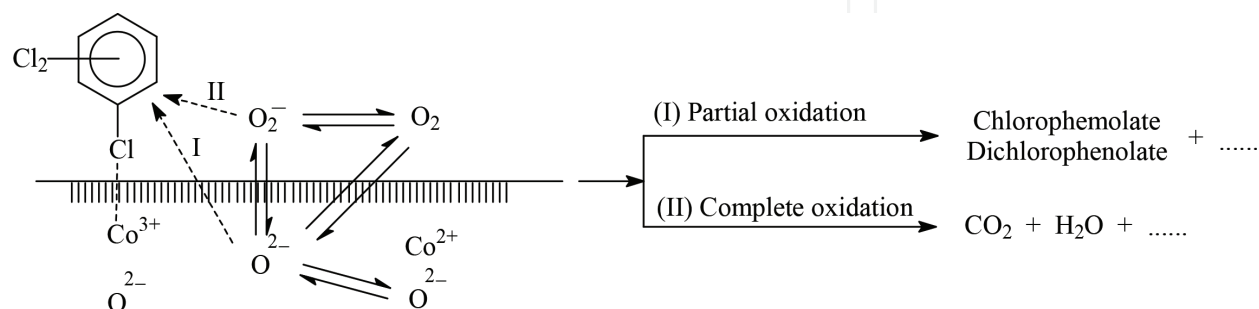
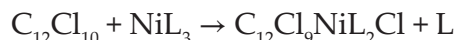
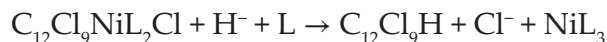


Figure 11. Oxidative attack mechanism for 1,2,4-trichlorobenzene degradation over cabbage-like Co_3O_4 [103].

2. Oxidative addition:



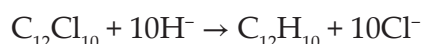
3. Reductive elimination:



4. Partial dechlorination:



5. Complete dechlorination



A study of polychlorinated biphenyls' reactivity in nucleophilic versus electrophilic substitutions demonstrated that S_N reactions are of the hard acid-hard base type [108], having a lesser probability to occur.

Meanwhile, several other procedures seem to favor the radicalic hypothesis: for example, PCBs are more rapidly hydrodechlorinated when in the presence of a mixture of persulfate and quinines, a system known to generate free radicals [109]. Ultrasonication of a polychlorinated biphenyls also seem to lead to a radicalic mechanism, since the first step is presented as a homolytic cleavage of the C-Cl bond [110].

Special attention must also be given to a new entry in panoply of degradation procedures: the mechanochemical approach in the hydrodechlorination/destruction of polychlorinated arenes [11]. The mechanochemical reactions imply activation of the chemical bonds through deformation under mechanical stress, leading to their rupture and subsequent reformation [111]. Even if most mechanochemical processes applied to polychlorinated aromatic compounds implied radical intermediates, it was not uncommon to consider the formation of ionic species. For example, Birke et al. suggested one reductive dechlorination process with alkali metals in the presence of hydrogen donors—the formation in the first step of a radical anion [112] (**Figure 12**):

Generally, the activation of the substrate takes place on the solid reagent, one of the most used being CaO [113–117]. After the cleavage of CaO crystals and the exposure of new surfaces, the

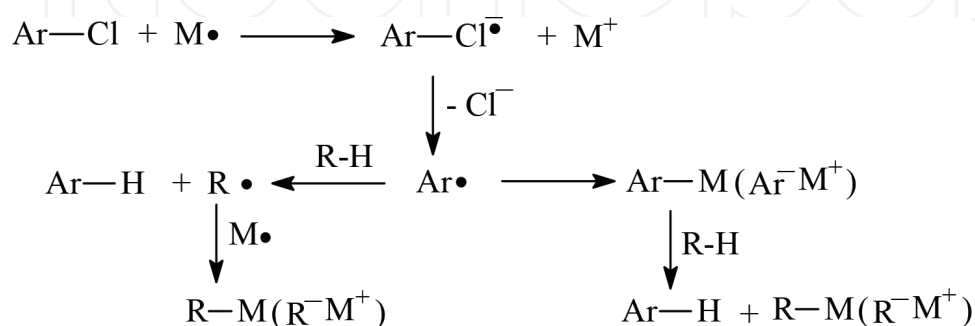


Figure 12. Reductive dechlorination of chlorinated aromatics (arylchlorides, Ar-Cl) by alkali metals in solution in the presence of hydrogen donors (R-H) like ethers or alcohols [112].

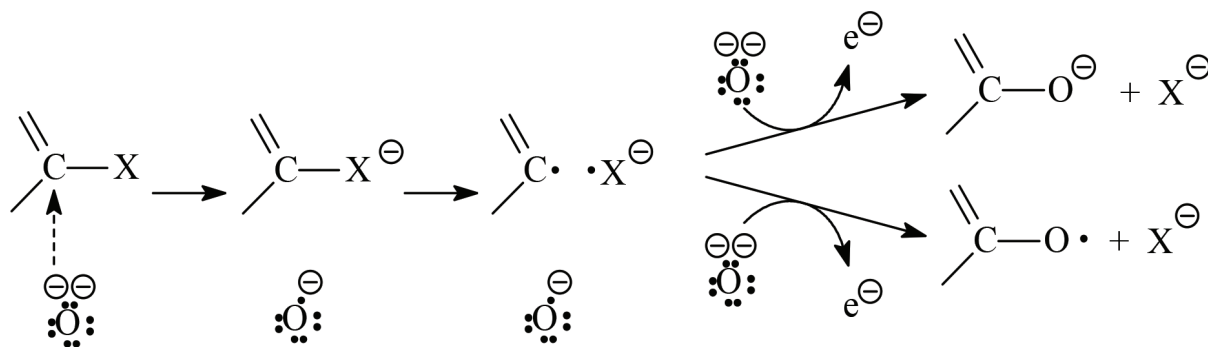


Figure 13. Dehalogenation mechanism with CaO [11].

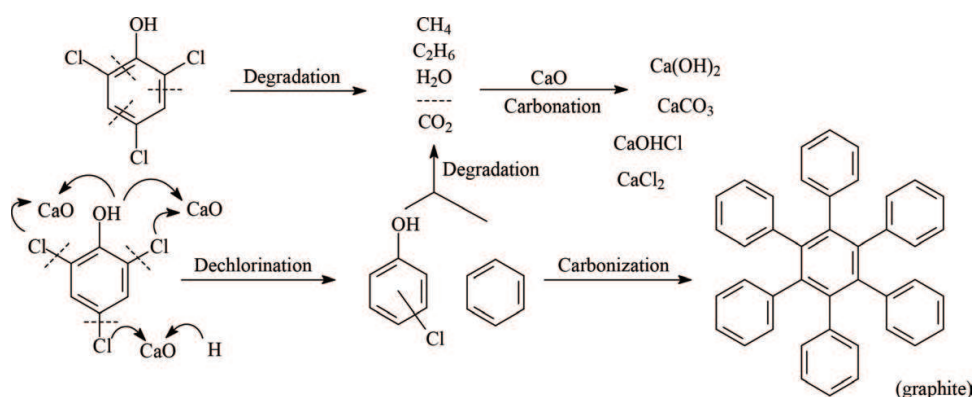


Figure 14. Degradation ways of 2,4,6-trichlorophenol in the mechanochemical reaction [117].

oxide ions are induced by mechanical activation to transfer an electron to pollutant's carbon atoms, thus generating an anion radical [11] (**Figure 13**).

The process does not even need the presence of a H donor, ultimate products being either oxidation one (e.g. CO_2) or of a graphitic nature – through carbonization processes [117] (**Figure 14**).

The addition to the reaction mixture of a good radical generator, such as SiO_2 , accelerates the carbonization process [115, 118, 119]. The presence of zero-valent metals in the ball-mill device may induce the formation of organometallic compounds of a Grignard type [120, 121].

3. Concluding remarks

Understanding the mechanism of a hydrodechlorination process is important only if the degradation products are organic compounds of lesser toxicity. If the destruction is complete, yielding CO_2 and various carbonaceous structures, the mechanism is less important.

Upon the main two hydrodechlorination paths (radical versus ionic), it can be observed that both may be encountered, but there seem to be more evidence for the first, although in many cases the first step is the formation of radical anion through single-electron transfer. The type of activation (chemical, photochemical, thermal, cavitation, or mechanochemical)

is instrumental in the type of reaction mechanism. Reaction conditions as well as reagents are also decisive in the type of mechanism the process will adopt. But through a better understanding of these aspects, a grasp on the reaction mechanism could be taken, and thus it could be possible to not only anticipate the advantages but also the limitations of a particular process. For example, when treating polluted soils with a mixture of Al and CaO, according to this type of mechanism, the presence of a hydrogen donor, namely soil moisture, is necessary [122]. Thus, it could be predicted that a soil too dry would be impracticable for treatment. On the other hand, many metallic systems can be effective even in the presence of large quantities of water [123], and even in aqueous media [124]. At the same time, the importance of the chemisorptions of hydrogen ions or nascent hydrogen on metallic surfaces has been understood, and the process can somehow be improved by the addition of stabilizers such as polyvinylpyrrolidone [125] or even biochar [126].

Thus, it will become easier to predict the successful outcome of a certain treatment process for a certain contaminated matrix (fly ash, soil, groundwater or wastewater) by considering the metallic system chosen, the moisture content (or the addition of any other potential hydrogen donor, in the form of an organic solvent—mainly alcohols), and the presence of a sorption substrate for the different forms of hydrogen transfer involved (even if it is only fly ash).

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