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Phase-transfer promotion of hydrodechlorination of chlorophenoxy-pesticides over Pd/C and Raney-Ni

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Abstract

Hydrodechlorination of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), pentachlorophenol (PCP), and *p*-chlorobenzoic acid with hydrogen gas over 5% Pd/C or Raney-Ni was studied in different liquid phase systems: (1) ethanol or ethanol–aqueous KOH; (2) in the multiphase system, composed by an organic phase and aqueous KOH and containing a quaternary ammonium salt (Aliquat 336). Under mild conditions (50 °C and atmospheric pressure of hydrogen) quantitative hydrodechlorination of 2,4,5-T is achieved in 1–4 h over Raney-Ni or Pd/C in the multiphase system or in the ethanol–aqueous KOH solution. PCP reacts selectively giving the dechlorinated phenolate in several hours in the system made of aqueous KOH (with Raney-Ni or Pd/C) or in several minutes in the presence of a small amount of Aliquat 336 solution in isooctane (1–4 molar% of Aliquat 336), where Aliquat 336 promotes the phase-transfer of polychlorinated anion. The reaction rates versus conditions, process localization, and the role of the ionic liquid environment are discussed.
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Keywords: 2,4,5-Trichlorophenoxyacetic acid; 2,4,5-T; Pentachlorophenol; PCP; *p*-Chlorobenzoic acid; Hydrodechlorination; Multiphase system; Phase-transfer; Supported ionic liquid; Aliquat 336; Pd/C; Raney-Ni

1. Introduction

We have previously reported on the applications of the multiphase catalytic hydrodechlorination (HDCl) of a number of toxic polychlorinated pesticides, such as lindane [1], dieldrin [2], DDT [2], as well as for other POPs, such as polychlorinated dioxins and furans [3] and PCBs [4] using Pd/C, Pt/C, and also Raney-Ni as catalysts, hydrogen at atmospheric pressure and at 50 °C.

The environmental hazard represented by polychlorinated pesticides has been widely outlined by EPA, UNEP, IHPA, and sustainable technologies for destruction of such waste are being extensively developed [5]. However, the commercialized techniques are usually harsh and many of them are based on oxidation processes. An alternative approach for polychlorinated waste treatment is reductive catalytic dechlorination, which leads to mineralization of chlorine, eliminates the risk of secondary contamination, and where the reaction products can be eventually reused.

A substantial knowledge based on the use of different catalysts, reaction systems, and reductants has been accumulated for the HDCl reaction [6]. Often, HDCl as well as other catalytic reduction reactions are studied with particular emphasis on their environmental application [7]. A novel catalytic methodology for organochlorine waste treatment lies in the promotion of HDCl by a quaternary ammonium salt [8], an effect that has been studied for over a decade since the first report [9]. Focus is placed on the exploration of chemical transformations of the substrates, in order to identify ways for their utilization/reuse, and not only for destruction.

The present study deals with the HDCl of two polychlorinated pesticides having an acidic function, namely

2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and pentachlorophenol (PCP). 2,4,5-T, which belongs to the family of chlorophenoxy herbicides, is the known defoliant "Agent Orange". Besides its intrinsic toxicity, technical 2,4,5-T contains high percentage of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD, formed as by product in the production of 2,4,5-T), which contributes to the toxicity of 2,4,5-T.

Pentachlorophenol is the most important compound in the group of chlorophenols, which have been used as preservative agents, disinfectants, herbicides, fungicides, and insecticides. The heavy chlorophenols are contaminated by polychlorophenoxyphenols, polychlorodibenzo-*p*-dioxins, and polychlorodibenzofurans (PCDD/Fs); obviously the higher chlorinated phenols have higher percentage of 17 toxic PCDD/Fs. PCP is more toxic than less chlorinated phenols, it is more lipophilic and accumulates in fatty tissues, it is more persistent in the environment (less biodegradable) and difficult to dechlorinate.

The studies on the catalytic hydrodechlorination of 2,4,5-T appear to be very scarce. Only biodegradation [10] and photodegradation [11] methods have been thoroughly studied, the latter, however, affords only partial dechlorination and leads to the formation of toxic 2,4,5-trichlorophenol. Among the electrochemical degradation methods for 2,4,5-T, both reductive [12] and oxidative [13] techniques have been reported. Catalytic hydrodechlorination of PCP was addressed in a number of studies, however, harsh conditions, e.g. elevated temperatures [14] or pressures [15] (unless more active reductants, like hydrazines are used) are usually employed.

The present study explores the reductive catalytic dechlorination of 2,4,5-T and PCP in various liquid phase systems: the multiphase system, mixed solvent systems, and water, in order to identify an alternative detoxification protocol (other than combustion). It also addresses the behavior of water and organic soluble aromatic chlorides, and in particular, the effects induced by their salification by KOH, formation of an ion pair with the quaternary ammonium salt, and their partition in the biphasic aqueous organic system.

The treatment of 2,4,5-T and PCP, and therefore of the less chlorinated products (e.g. 2,4-D, less chlorinated phenols, etc.) under the multiphase conditions, should eliminate also the toxicity due to their impurities (e.g. 2,3,7,8-TCDD in 2,4,5-T), as indicated by our previous studies on the HDCl of toxic dioxin and furan mixtures [3]. It should be especially stressed that the combustion of these toxicants is very undesirable since it would lead to the formation of the very toxic 2,3,7,8-TCDD. Other methods, preferably reductive, should therefore be sought for their disposal.

2. Experimental

All the reagents and solvents were used as purchased without further purification. Raney-Ni (50% slurry in water) was from Engelhard, Actimet M^{TM} (Ni 93% and Al 7%, particle size distribution of 0–80 μm, surface area of 70–80 m^2/g). Pd/C (5%) was from Aldrich, Art. no. 20,568-0. Aliquat 336$^{®}$ (tricaprylmethylammonium chloride) and 2,4,5-T (97% pure), PCP (99% pure), and *p*-chlorobenzoic acid (99% pure) were from Aldrich. GC analyses were performed on a Varian 3400 using a fused silica capillary column "Chrompack CP-Sil 24 CB lowbleed/MS" (30 m × 0.25 mm, film thickness 0.25 μm). GC/MS analyses were performed on an Agilent 5973 mass detector coupled to an Agilent 6890N GC with an HP-5MS capillary column (30 m × 0.25 mm, film thickness 0.25 μm). HPLC analyses were performed on a Varian 9010 coupled with a Varian 9050 UV detector, using a Bondesil^{TM} C8 column (10 cm × 4.6 mm, film thickness 5 μm), eluted with a mixture of MeCN 32%, H$_2$O 66%, and AcOH 2% at 1.2 mL/min.

2.1. General procedure for the reaction of 2,4,5-T

A 25 mL three-necked round-bottomed reactor with a water jacket heated at 50 °C, supplied with a tube for hydrogen supply, a condenser, was loaded with 10 mL isooctane solution, if not otherwise indicated, containing 0.0179 g (0.07 mmol) of 2,4,5-T, 0.103 g (0.26 mmol) of Aliquat 336, and 0.0455 g of 5% Pd/C (0.02 mmol Pd) or 0.25 g of the Raney-Ni slurry (2 mmol Ni). Aqueous KOH solution (5.7 mL) was added therein. When the reactions were run in EtOH–H$_2$O, 10 ml solution of 0.179 g (0.7 mmol) of 2,4,5-T, and of all of the above, including KOH and containing the catalyst, in a 1:1 mixture of ethanol and water was used instead, if not otherwise indicated (see Tables).

2.2. General procedure for the reaction of PCP

The reactions were run in a 25 mL three-necked round-bottomed reactor heated at 50 °C with a water jacket, supplied with a tube for hydrogen supply, and a water condenser. If indicated, 10 ml of isooctane or the required volume of isooctane solution of Aliquat 336 (0.116 g, 0.26 mmol) or Aliquat 336 alone (see conditions given in text) and the heterogeneous catalyst (0.0455 g of 5% Pd/C, 0.02 mmol Pd or 0.25 g of 50% Raney-Ni slurry in water, 2 mmol Ni) were introduced in the reactor and stirred for 3–5 min. Thereafter, 10 ml of PCP (0.187 g, 0.7 mmol) solution in 7% aqueous KOH was added.

The reaction procedure for *p*-chlorobenzoic acid was the same as that for PCP, with the only difference that 1% KOH solution of 0.238 g (0.7 mmol) of *p*-chlorobenzoic acid was added in the reactor.

All the components loaded, the reaction was run, stirred magnetically at 1000 rpm, and thermostated at 50 ± 1 °C, bubbled with H$_2$ at atmospheric pressure at 10 mL/min. The samples were collected from the organic phase during the reaction at time intervals, and analyzed by means of GC, GC–MS, or HPLC. About 20 μL of the organic phase

of reaction mixture was taken for each sample, which was then diluted with ethyl ether up to 1–2 ml or with acetone or ethanol, if the latter was the solvent. Before injection, the samples were shaken with silica to remove Aliquat 336, and/or filtered through Whatman filter to remove catalyst. The samples in ethanolic KOH or ethanolic-aqueous KOH solution were neutralized with aqueous HCl. In case of HPLC samples, these were dissolved in nine volumes of a mixture of MeCN and AcOH. For the reaction of PCP the samples were taken from the aqueous phase and then introduced with HCl and ethyl ether phase to extract phenols; after that the ether phase was analyzed by GC–MS.

The quantitative analyses of the reaction mixture for PCP experiments were determined by measuring the percent ratio of MS total ion peaks areas of the analyzed compounds. In case of HPLC analyses for 2,4,5-T, the absolute calibration was used, where the calibration coefficients (determined for separately prepared compound solutions) for 2,4,5-T, isomers of di- and mono-chlorophenoxyacetic acids, and for phenoxyacetic acid were calculated as follows: 846, 856, 867, and 1500 [V s L mol^{-1}] ($C = S/k$, for 10-times diluted samples injected through the 10 μL loop). For *p*-chlorobenzoic acid, both aqueous and organic phases were analyzed by HPLC and, given equal volumes of these two, the peak areas of the same components found in different phases were combined, and on this basis the ratio of these components (substrate and dechlorinated acid) was calculated. Thus, the concentrations reported in tables for all substrates are meant to be percentage of the initial substrate amount. The initial rate, where reported, was determined by the linear fitting of the concentration–time data in the initial part of kinetic curves (normally up to 30%, or where still a good linearity of the curve was observed).

The *X*-value reported in Tables 1 and 2 for 2,4,5-T reaction is the dechlorination degree, which is calculated as follows:

$$X = 1 - \frac{\sum_{i=0}^{j} iC_i}{jC_0}$$

$\times \, 100\%$ (or reported total percent of components)

where C_i is the molar concentration of a substrate containing i chlorine atoms in the molecule, j is the initial number of chlorine atoms in the molecule, and C_0 is the initial concentration of the dechlorinated compound.

Table 2
Hydrodechlorination of 2,4,5-T in EtOH/water (1:1) 7% KOH solution

No.	Catalyst	Aliquat 336	Time (min)	Conversion (%)	X (%)	Yield (% HPLC)		
						2	3	4
1	5% Pd/C	No	73	100	100	0	0	100
2	Raney-Ni	No	230	100	100	0	0	100
3	5% Pd/C	1 Equivalent	150	100	81	5	48	47
4	5% Pd/C	2 Equivalent	160	100	95	0	15	85

3. Results and discussion

3.1. Hydrodechlorination of 2,4,5-T over Pd/C and Raney-Ni in the multiphase system

HDCl of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T, **1**) has been studied over both Pd/C and Raney-Ni and in both biphasic aqueous – isooctane and ethanol – aqueous media in the presence of KOH. In all cases, the reaction proceeded via three consecutive dechlorination steps (see Scheme 1) giving the fully dechlorinated acid **4** and/or its potassium salt (see data in Tables 1 and 2). Two reaction intermediates, dichloro- and monochloro-derivatives **2** and **3**, were also monitored by HPLC, but their isomers could not be resolved. No other products, i.e. those resulting from C–O bond hydrogenation, aromatic ring reduction, or reduction of carboxylic function were observed.

It has been found that the presence of Aliquat 336 in the biphasic aqueous KOH – isooctane system increases the solubility of the acid dramatically due to the formation of the ion pair of Q$^+$ and 2,4,5-T anion. 2,4,5-T in its acidic form is practically insoluble in isooctane as no solubilization was visually observed at attempt to dissolve 0.018 g (0.07 mmol) of the acid in 10 ml of isooctane. Neither could this amount be dissolved in 10 ml of aqueous KOH. However, it dissolves in 10 ml of isooctane in the presence of 0.26 mmol of Aliquat 336 (standard amount of Aliquat 336 used in the multiphase system, see entries 1, 3, 4 of Table 1). A 10-fold excess of the acid (0.18 g, 0.7 mmol standard concentration) can be dissolved in the same volume of isooctane in the presence of 4 equivalents of Aliquat 336 (1 mmol, see entry 2). In this case, the ion pair [2,4,5-T$^-$Q$^+$] resides exclusively in the isooctane phase of the biphasic aqueous KOH–isooctane system, since neither the solubility of 2,4,5-T nor that of its salt in water (280 mg/L for the acid, and less than 1 g/L for the salt) are comparable with that of [2,4,5-T$^-$Q$^+$]

Table 1
Hydrodechlorination of 2,4,5-T in isooctane/aqueous KOH in the presence of Aliquat 336

No.	Substrate (mol/L)	Catalyst	KOH (%)	Aliquat 336	Time (min)	Conversion (%)	X (%)	Yield (%, HPLC)		
								2	3	4
1	0.007	5% Pd/C	2	1 Equivalent	210	99	97	1	4	94
2	0.07	5% Pd/C	7	4 Equivalent	50	100	100	0	0	100
3	0.007	Raney-Ni[a]	2	1 Equivalent	550	86	81	5	6	75
4	0.007	Raney-Ni	2	1 Equivalent	210	84	79	5	5	74

[a] 0.025 g 50% slurry in water.
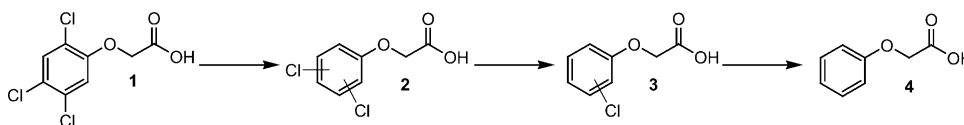
Scheme 1. Hydrodechlorination of 2,4,5-T.

in isooctane. HPLC analyses have indicated the presence of only traces of 2,4,5-T anion (as well as of the reaction products, which are less chlorinated derivatives **2**, **3**, and **4**) in the aqueous phase with respect to the amount present in isooctane.

The results on the HDCl of 2,4,5-T in the multiphase system in the presence of Aliquat 336 are presented in Table 1. Three experiments (entries 1, 3, and 4) have been carried out with 0.007 M 2,4,5-T, and 0.026 M Aliquat 336, 10 times less substrate than that normally used in the multiphase system, e.g. in the experiments with PCP (see below). In addition, to achieve sufficiently fast reaction, the Pd–substrate molar ratio was increased 10 times, i.e. up to 30% for Pd/C (0.0455 g 5% Pd/C, entry 1) or nearly 3000% for Raney Ni (0.25 g of 50% slurry, entry 4). The reaction with Raney-Ni (entry 4) is slower than that over Pd/C (entry 1), and decreasing the amount of Ni 10-fold (entry 3) renders the reaction even slower, where no complete conversion is observed even after 9 h of reaction. The most efficient system is that with a four-fold excess of Aliquat 336 (1.04 mmol) and a standard 0.7 mmol amount of substrate where notwithstanding the 3% Pd–substrate molar ratio (0.045 g of Pd/C) the reaction is complete in 50 min (entry 2). From all evidence, besides the effect of Aliquat 336 on the solubility of 2,4,5-T, there is also an acceleration of HDCl owed to the presence of Aliquat 336, i.e. the usual HDCl promotion effect of Aliquat 336 in the multiphase systems.

3.2. Hydrodechlorination of 2,4,5-T over Pd/C and Raney-Ni in ethanol–aqueous system

Another way to facilitate the reaction of 2,4,5-T is by using an ethanol–aqueous base solution. In a mixture of ethanol–water (1:1) both the acid and its salts are soluble. In pure ethanol, however, only 2,4,5-T is soluble at the working concentration of 0.07 M, but in the presence of KOH the potassium salt formed precipitates immediately. The reaction of 2,4,5-T in 10 ml EtOH–H$_2$O has been studied with standard amounts of substrate (0.7 mmol) and catalyst (0.0455 g and 0.25 g of Raney-Ni slurry). The results of Table 2 show that the reaction in such a system is the same or more efficient than in the biphasic system (Table 1), and the quantitative dechlorination yields are achieved in very short times with either Pd/C or Raney-Ni (entries 1 and 2). The generally higher activity of the mono-phase system is probably a result of easier neutralization of HCl, while in the multiphase system the transport processes through the interface comes into play, there is no evidence of EtOH

acting as a proton source although this is also a possibility [16].

In the presence of 0.026 M of Aliquat in the EtOH–H$_2$O system the reaction of 2,4,5-T is slower then in the absence of Aliquat 336 (entry 3). In this case, the full conversion of 2,4,5-T is achieved in rather short times, but the dechlorination of monochlorinated intermediate acid does not seem to proceed too rapidly as it is in other experiments. As a rule, less chlorinated aromatic analogues react more promptly, as has been observed in the reactions of various polychlorinated benzenes under multiphase conditions, and 2,4,5-T, as well.

One may suggest that formation of the ion pair [2,4,5-T$^-$Q$^+$], if formed in the EtOH–H$_2$O system, can have a negative effect, e.g. by bringing the 2,4,5-T away from the catalyst surface. According to the proposed mode of action of ammonium salts in the multiphase system, their promotion of the reaction is connected to the formation of the Aliquat 336 layer on the catalyst surface, where the reaction takes place. This layer is seen in non-polar solvents, like isooctane where given also the presence of the aqueous phase, Aliquat 336, after having absorbed a certain amount of water, separates out as a third liquid phase [8]. In EtOH, Aliquat 336 is well soluble and, as a rule, does not have any effect on the reaction [17], probably because it stays in the bulk and does not tend to adsorb on the surface of catalyst and liquid–liquid interface.

However, doubling the amount of Aliquat 336 increases the conversion at time reported in the EtOH–H$_2$O system (entry 4). Probably, at higher concentrations the presence of Aliquat 336 on the catalyst surface rises, so its promotion effect becomes sensible also in this case.

The proposed approach must be also applicable for the remediation of aqueous solutions of 2,4,5-T, e.g. of the aqueous waste resulting from the base treatment of contaminated soils. However, the instrumentation restrictions did not allow analysis of low concentrated aqueous solutions of 2,4,5-T in our case. Nevertheless, some preliminary conclusions on such possibility can be made, for example, considering the hydrodechlorination of *p*-chlorobenzoic acid, which is better soluble in water and aqueous base than 2,4,5-T. The reaction of *p*-chlorobenzoic acid was studied over Pd/C under the same conditions as with 2,4,5-T. In the aqueous system (10 ml of 1% KOH solution) *p*-chlorobenzoic acid was dechlorinated in 35 min over Pd/C. Under the conditions of entry 2, Table 1 (with the only exception that 10 ml of 1% KOH in water was used), the reaction of *p*-chlorobenzoic acid gave 96% of benzoic acid (by HPLC) already in 15 min and full dechlorination was observed in 20 min.

3.3. Hydrodechlorination of pentachlorophenol

Contrary to 2,4,5-T, in the biphasic isooctane–aqueous KOH system PCP is present preferably in the aqueous phase in the form of its potassium salt. It is known that chlorophenolates are highly soluble in water (over 200 g/L) and are insoluble in apolar solvents, e.g. in benzene [18] and that less chlorinated phenols are more hydrophilic. The presence of Aliquat 336 in the biphasic system (10 ml isooctane, 10 ml 7% aqueous KOH) does not seem to affect the partitioning of PCP, which was not detected in the organic phase in sensible amounts.

The heterogeneous hydrodechlorination of PCP in the aqueous KOH system, over Raney-Ni or 5% Pd/C proceeds to phenol (Scheme 2) with quantitative yields in 8 and 3 h, respectively (see Fig. 1). As one can see from the kinetic profiles the reaction does not exhibit any significant inhibition within the reaction time studied. It is also noticeable that only one intermediate, TeCP is observed (the other less-chlorinated phenols were not present in more than 1% and were not quantified), where its quantity is very small (around 5% maximum) in the reaction over Pd/C and reaches 70% in the reaction over Raney-Ni. This is indicative of the fact that the first hydrodechlorination step of PCP is the rate-limiting over Pd/C and that the successive HDC steps are either too fast, where the rate grows from any preceding to the successive step (as was previously observed for other polychlorinated aromatics [17]), or that the intermediates, such as TeCP and the less chlorinated ones are bound so strongly to the surface that they do not desorb from the active site before undergoing further transformation. These two options support each other since the absence of intermediates could result from both their high reaction rates and their high surface affinity. Other authors have studied the Ni catalyzed hydrodechlorination of 2,3,5-TCP, and also showed that the consecutive HDCl is faster than the concerted process [19].

The direct reaction of polychlorinated substrates without desorption–adsorption of intermediates was observed also in some other kinetic studies on heterogeneous catalytic hydrodechlorination of polychlorinated aromatics [20]. The strength of adsorption results often into unusual kinetic behavior of reacting species, when, instead of competitive reactions of several reacting substrates [9,21], or substrates and intermediates, a series of consecutive reaction occurs, where the ones with higher adsorption affinity react first, and only after their reaction is complete the catalyst surface is made available for the reaction of the others. Similar
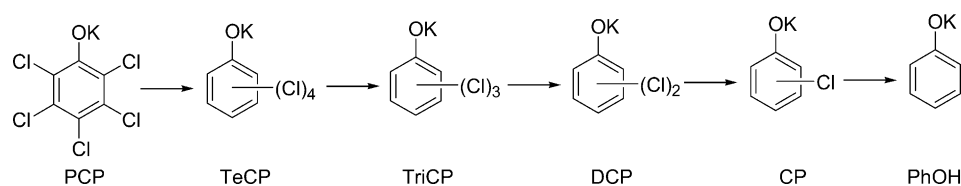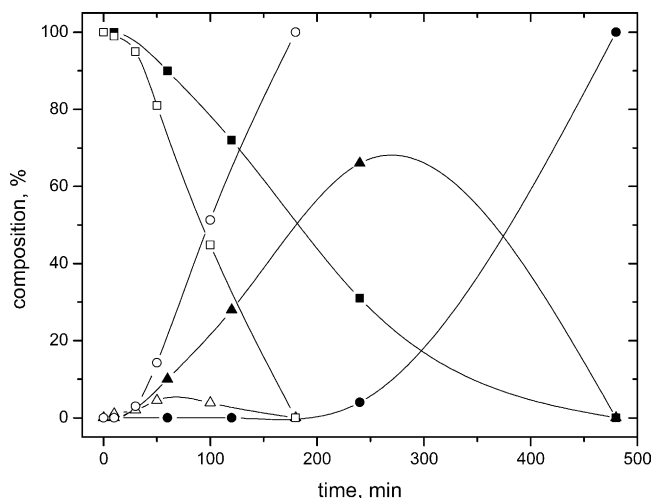

Fig. 1. Hydrodechlorination of PCP in the 7% KOH aqueous solution over Pd/C (open symbols) and Raney-Ni (solid symbols). (■ and □), PCP; (▲ and △), TeCP; (○ and ●), PhOH.

phenomenon is observed in the reaction of PCP over Raney-Ni (see Fig. 1), where formation of phenol is unusually suppressed in the initial reaction period, when there is PCP present, but thereafter the rate of phenol accumulation becomes similar or even faster then that of PCP consumption in the initial period. This suggests that the adsorption of PCP is stronger than that of TeCP, so that the latter cannot react when there is still high concentration of PCP. Another notable fact is that in all the systems considered in this study PCP was never consumed before TeCP, even if the latter was present in high concentrations, which suggests that the reduction of TeCP must be fast, but it is inhibited by the presence of PCP. On the contrary, the adsorption of less chlorinated phenols than TeCP must be strong, and not weaken with decreasing chlorination degree, otherwise their reactions would be inhibited by their precursors, which is not so.
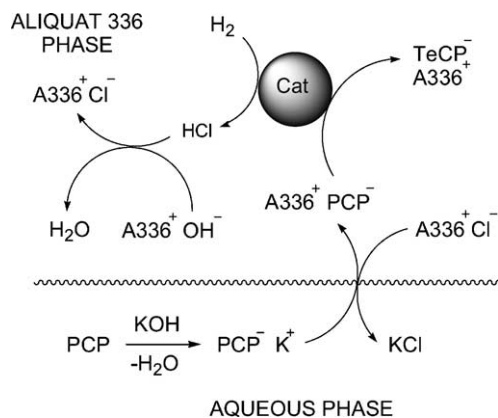
Even though PCP is present as salt in the aqueous phase in the biphasic isooctane–aqueous KOH system, it was found that PCP reacts faster in the presence of the organic phase and Aliquat 336. The reaction of PCP in the multiphase system, namely in the presence of 3 ml 0.087 M solution of Aliquat 336 in isooctane, and under the same other conditions as in the aqueous system described above, is complete in 50 min on Pd/C and in 40 min on Raney-Ni. Interestingly, only in the reaction of PCP over Pd/C in the isooctane–aqueous KOH system were less chlorinated intermediates (mono-, di-, and trichlorophenol)

Scheme 2. Hydrodechlorination of pentachlorophenol.

observed, whose concentrations were similar, but did not exceed 10% of the initial substrate concentration.

An explanation for the increased catalytic activity of the biphasic system with Aliquat 336 lies probably in the phase-transfer of PCP anion to the organic phase (see Scheme 3). The supported Pd or Raney Ni in such system stay preferably in the organic phase and on the surface, surrounded by the liquid layer of Aliquat 336 [8]. Even though the partition coefficient for PCP is small and its concentration is very low in the organic phase, the rate acceleration can have rather kinetic nature. Assuming that the transfer of the ion pair of PCP anion with the quaternary cation of Aliquat 336 from the aqueous phase to the organic phase and to the catalyst surface is fast, the rate can still be very high.

Moreover, the effect of Aliquat 336 and of the ionic environment surrounding the surface should also favour the reaction, since the concentration of PCP anionic species in the immediate vicinity to the catalyst surface is expected to be high in this case. The transfer of PCP–Aliquat 336 ion pair from aqueous KOH to the phase made by Aliquat 336 should also be more favourable energetically than that to isooctane. Several of our former studies have shown that catalytic reactions on Pd/C often proceed faster in a pure Aliquat 336 made phase, which is an ionic liquid. In the present case, however, the reaction of PCP in this system appeared quite slow (see Fig. 2) in the system made of aqueous KOH–PCP, Raney-Ni and pure Aliquat 366, probably due to the mass transfer inhibition, since Aliquat 336 is very viscous. It is also shown in Fig. 2 that with the addition of isooctane in the aqueous KOH–Aliquat 336 system the rate increased significantly. The rate in the system with aqueous KOH and pure Aliquat 366 was even slower than in the system without Aliquat 336, which is because the Aliquat 336 phase extracts the catalyst from the aqueous phase, therefore deactivating a bigger part of it.

The effect of Aliquat 336 on the reaction was further investigated by exploring the same reaction of PCP over Raney-Ni in the systems with different amount of isooctane, and with fixed amounts of PCP, KOH, and Aliquat 336. The initial rates of PCP consumption against the Aliquat
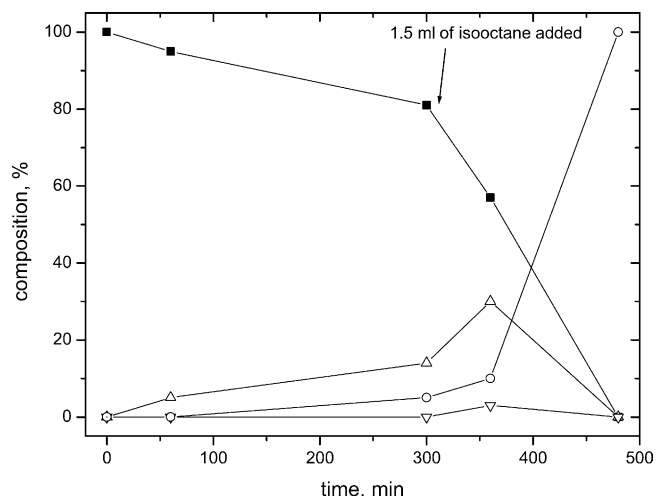

Fig. 2. Kinetic profiles of PCP hydrodechlorination over Raney-Ni in the 7% aqueous KOH–Aliquat 336 biphasic system, where 1.5 ml of isooctane was added after 310 min of reaction time. (■), PCP; (△), TeCP; (▽), TCP; (○), PhOH.

Scheme 3. Scheme of phase-transfer promotion of the hydrodechlorination of PCP in the Aliquat 336 layer.

336–isooctane ratio in the organic phase, obtained from these experiments are plotted in Fig. 3. The horizontal line on the plot indicates the initial rate of PCP reaction over Raney-Ni observed in the pure aqueous KOH system, described above. There is an optimal Aliquat 336–isooctane ratio between 1 and 4 molar% of Aliquat 336 (the highest rate shown in Fig. 3 corresponds to around 0.04 g/ml concentration of Aliquat 336 in isooctane) where the maximum rates are expected. This optimum implies a situation when there is sufficient amount of isooctane to achieve good catalyst dispersion and high mass-transfer coefficient, but where the amount of Aliquat 336 is still high enough to provide transfer of PCP anions to the catalyst surface.

It is worth noting that even in the reaction with pure isooctane, i.e. when there is no Aliquat 336 (in this case, Raney-Ni stays preferably on the aqueous–organic inter-face), the reaction is still much faster than that in just aqueous KOH (see Fig. 3). This fact supports our previous observations, when the activity of Raney Ni in the multiphase system decreased sharply, if the latter was put in the system together with aqueous KOH [17]. Instead, if Raney-Ni was introduced together with the organic phase and preagitated for 3–5 min before the aqueous KOH was added therein, good catalytic activity was maintained through all the reaction. Similar result was obtained for the reaction under study in the aqueous KOH–Aliquat 336–isooctane system, which was conducted (1) with preagitat-ing Raney-Ni in aqueous base, and (2) in the organic phase (isooctane with Aliquat 336) before starting the reaction (see Fig. 4); the rate was 3–4 times faster in the latter case. All this suggests that the activity of Raney Ni in hydrode-chlorination is increased in the organic environment and instead, suffers from the presence of aqueous KOH. This conclusion is apparently strange since Raney-Ni is originally
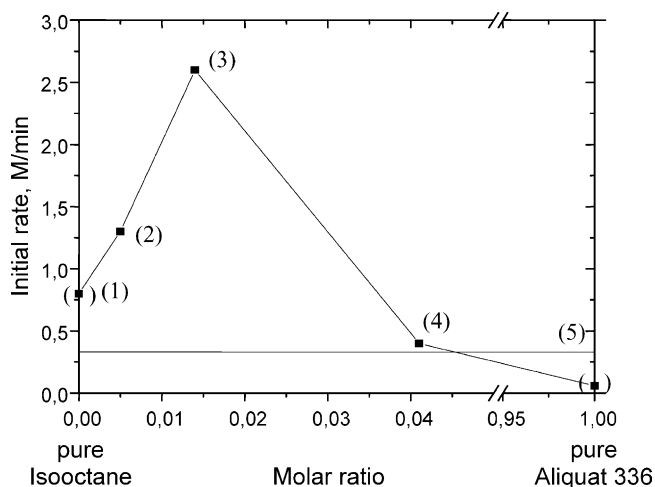
Raney-Ni than on Pd/C (other conditions being equal) which means that aside from possible phase-transfer effects produced by Aliquat 336, there is obviously a direct effect on the catalyst, at least in the case of Raney-Ni.

4. Conclusions

2,4,5-T is reduced to phenoxyacetic acid in quantitative yield over either 5% Pd/C or Raney-Ni in the multiphase system or in EtOH–H_2O systems with KOH.

The presence of Aliquat 336 in the multiphase system in excess with respect to 2,4,5-T is required in order to achieve solubility of 2,4,5-T in the organic phase, which is increased dramatically owing to the formation of the ion pair of 2,4,5-T anion with the quaternary cation of Aliquat 336. Increasing the amount of Aliquat 336 with respect to the amount of Pd/C yet increases the rate of dechlorination due to the known promotion effect of an onium salt of the HDCl of aromatic chlorines under multiphase conditions.

Alternatively, good solubility of 2,4,5-T can be achieved on the basic medium EtOH–H_2O. This system also affords full and rapid dechlorination with Pd/C or Raney-Ni, however, the presence of Aliquat 336 is undesirable because it lowers the reaction rate and decrease the degree of dechlorination. This again confirms that the role of Aliquat 336 as of a promoter of HDCl is manifested only in the multiphase systems, where it is less soluble and therefore tends to form a distinct liquid layer supported on the catalyst surface, where the reaction proceeds.

The potassium salt of PCP is quantitatively dechlorinated to the phenolate over Pd/C or Raney-Ni in the 7% aqueous KOH solution or in the biphasic aqueous–organic system with Aliquat 336. It was suggested that the adsorption of PCP-K on the catalyst is stronger than that of less chlorinated phenolates, however, the latter ones react faster as their chlorination degrees decrease, which results in the absence of intermediates containing from one to three chlorines in the reaction mixture.

It was found that PCP reacts easier in the system containing also the organic phase made of isooctane and Aliquat 336, even though no detectable amounts of PCP were found in this phase. The rate acceleration is achieved at a certain ratio of isooctane and Aliquat 336 in the organic phase, which seems to be conditioned by the conjunction of a promotion effect of Aliquat 336 on the one hand, and by its restriction of mass-transfer (if taken in excess) on the other. The promotion of the reaction in the presence of Aliquat 336 is most likely due to the formation of the PCP–Aliquat 336 ion pair and its phase-transfer to the organic phase and to the catalyst surface; in addition, the formation of an ionic liquid environment made by Aliquat 336 coating the metal catalyst surface (e.g. as suggested for halobenzenes) may be another contribution to the increased catalytic activity in this case.

It has been also noted, as it was in the previous studies, that the activity of Raney-Ni in hydrodechlorination in the

Fig. 3. Initial rate of PCP hydrodechlorination plotted against the Aliquat 336–isooctane ratio in the system made of 10 ml 7% aqueous KOH, 0.25 g of Raney Ni and: (1) 10 ml pure isooctane; 0.116 g of Aliquat 336 in: (2) 10 ml, (3) 3 ml, (4) 1 ml of isooctane, or (5) without isooctane.

present in aqueous KOH. However, it seems to loose water and gain lipophilicity if preagitated in the organic phase. The best effect is obtained in the presence of Aliquat 366 which makes it disperse finely in the organic phase, while in the absence of Aliquat 336, the catalyst is aggregated. If no such pretreatment is made, Raney Ni remains in the organic phase. The affinity of Aliquat 336 for the catalyst was noted also when pure Aliquat 336–aqueous KOH system was used (see above).

Notable fact is that the reaction over Raney-Ni in the multiphase system is one order of magnitude faster than that in aqueous KOH, while the reaction over Pd/C gains only three-fold rate increase (see above). This means that the effect of the multiphase environment is more pronounced on
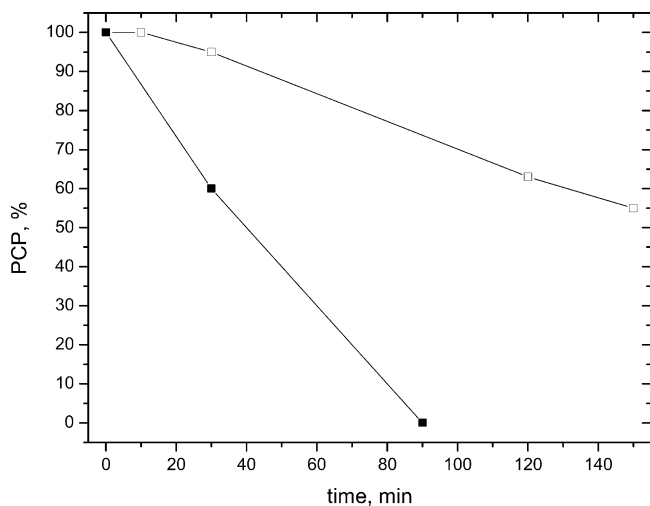

Fig. 4. Consumption of PCP in the 10 ml isooctane–10 ml aqueous KOH system in the presence of 0.7 mmol Aliquat 336 with (1) (■:), Raney-Ni pretreated in isooctane–Aliquat medium; (2) (□), Raney-Ni pretreated in aqueous KOH.

biphasic aqueous basic–organic system is increased if it is pretreated in the organic phase before the reaction. Instead, if Raney-Ni is initially present in the basic aqueous phase, its activity decreases, seemingly because its transport to the organic phase is restricted.

In any case, these results on PCP HDCl show that even if the catalyst works in the aqueous phase, its activity can be substantially increased (up to one order of magnitude) if the reaction is localized in the organic phase, which contains Aliquat 336. This observation offers a convenient approach for the treatment of PCP contaminated waters. Separation of the aqueous phase, which contains PCP and all its products, from the organic phase, which contains just the catalyst and promoter and is easily separable (in case when there is Aliquat 336 it does not allow the catalyst go to the aqueous phase), is a strong engineering advantage.

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