Dechlorination of lindane in the multiphase catalytic reduction system with Pd/C, Pt/C and Raney-Ni

Sergei S. Zinovyev [a], Natalia A. Shinkova [c,1], Alvise Perosa [a], Pietro Tundo [b,*]

[a] *Interuniversity Consortium "Chemistry for the Environment" (INCA), Dorsoduro 2137, 30123 Venezia, Italy*
[b] *Ca' Foscari University of Venice, Dorsoduro 2137, 30123 Venezia, Italy*
[c] *N.D. Zelinsky Institute of Organic Chemistry of Russian Academy of Sciences, Leninsky pr. 47, Moscow 119991, Russia*

Abstract

Dechlorination of γ-hexachlorocyclohexane (lindane) is carried out in the multiphase catalytic system, composed by isooctane and aqueous KOH phases, a phase transfer agent (Aliquat 336) and a metal catalyst, e.g. 5% Pd/C, 5% Pt/C, or Raney-Ni. At 50 °C and atmospheric pressure the full conversion of lindane to 1,2,4-tricholorobenzene (1,2,4-TCB) is achieved in 5–10 min via the base assisted dehydrochlorination, followed by the metal catalyzed hydrodechlorination with hydrogen to benzene. Aqueous KOH and Aliquat 336 strongly affect the reaction: if present together they co-promote both dehydrochlorination and hydrodechlorination steps; if KOH is absent, the reaction is forced to follow a different catalytic pathway, which involves a removal of a pair of chlorines at every reaction step by zerovalent metal followed by reduction of metal with hydrogen. This is proven by the formation of 3,4,5,6-tetrachlorocyclohex-1-ene and 5,6-dichlorocyclohexa-1,3-diene as intermediates in the reaction over Raney-Ni, and by the absence of TCBs in the reactions on all the catalysts studied. The final yield of benzene via this pathway can be achieved in shorter times than in a system with KOH. The presence of Aliquat 336 in the isooctane-water system produces a 10-fold rate increase, the presence of alkaline water is also important since it avoids catalyst poisoning by neutralizing the hydrochloric acid formed.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Lindane; Hexachlorocyclohexane (gamma); Dehydrochlorination; Hydrodechlorination; Detoxification; Multiphase system; Aliquat 336; Pd/C; Pt/C; Raney-Ni

1. Introduction

Lindane, the γ-isomer of hexachlorocyclohexane (HCH, Fig. 1), is a heavily used insecticide, used on fruit, vegetables, and forest crops. It is also used in many countries as a topical treatment for head and body lice and scabies, a contagious skin disease caused by mites. Its possible carcinogenic effects on humans remain to be unequivocally demonstrated, but it appears on the CERCLA Priority List of Hazardous Substances, a list of substances which are determined to pose the most significant potential threat to human health due to their known or suspected toxicity and potential for human exposure, to their persistence in the environment, and potential to bioaccumulate [1]. Till

now, lindane alone and technical HCH (containing also α-, β-, and δ-HCH [2], the so-called "non-toxic isomers") have been widely used in agriculture [3]. The technical HCH mixture consists of 65–70% α-HCH, 7–10% β-HCH, 14–15% γ-HCH and 6–10% δ-HCH; since the forties, it has been produced hundreds of tons per year over the world. Technical HCH and lindane are now regulated in most European countries and North America [4].

The tons of HCH produced over the past years and stored nowadays represent an environmental danger and therefore have to be disposed of. The cheapest method for elimination of lindane and its wastes, combustion, is undesirable, because of the formation of even more toxic polychlorinated dioxins [5]. Alternatively, disposal of lindane and its conversion to more useful chemicals, can be carried out via chemical or biotransformations. As long ago as in 1871, Zinin reported on the reduction of HCH to benzene with metallic Zn in ethanol [6]. Lindane and its isomers can undergo the dehydrochlorination (DHC) reaction to

---

* Corresponding author. Tel.: +39-041-2348642;
fax: +39-041-2348620.
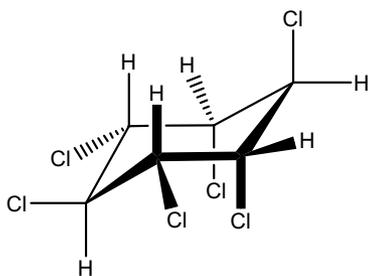*E-mail address:* tundop@unive.it (P. Tundo).
[1] On leave.

Fig. 1. Stereo conformation of γ-hexachlorocyclohexane (lindane).

form tricholorobenzenes (TCBs) either by thermal or the base-assisted processes [7–10]. The latter is more selective and can be carried out under mild conditions in the presence of a phase-transfer (PT) catalyst and an aqueous base [9,10]. Electrochemical [11] and bacterial [11–13] processes of HCH or lindane degradation are known and afford benzene. Lindane decomposition via sonochemical [14] or gamma ray [15] induced dechlorination/destruction has also been demonstrated. It has been reported recently [16] that lindane undergoes the processes of dehydrochlorination and hydrolysis in subcritical water to give less chlorinated benzenes, phenols, and phenol as the major final product. The use of just water under comparatively mild conditions (100–250 °C and the corresponding equilibrium pressures) is attracting, however, the drawback is low selectivity and formation of toxic chlorinated phenols as byproducts.

Few studies have been dedicated to the catalytic reduction of lindane over metal catalysts. The advantages that the heterogeneous catalytic processes can offer for utilization of toxic substances are both environmental and commercial (milder conditions, elimination of toxic and expensive reagents, ease of catalyst/product separation, good selectivity and yields). Schüth has reported [17] on the reductive dechlorination of lindane in hydrogen-saturated water over Pd/Al$_2$O$_3$. The reaction was shown to give benzene with 99% yield within 18 min at room temperature and atmospheric pressure, however, a 13-fold molar excess of Pd with respect to the substrate was used. The catalytic reduction (e.g. with hydrogen) of lindane is intriguing, since benzene and not cyclohexane (as expected from a regular DHC) is formed. However, no conclusions on the reaction mechanism have been made and no intermediates were observed. Destruction of lindane via catalytic or electrochemical processes appear to be more effective, also because the full mineralization of chlorine is achieved, whereas in the DHC reaction still toxic TCBs are formed.

Previously, we have reported on a number of applications of the multiphase catalytic systems for various catalytic reduction reactions [18–26], in particular, for the HDC of chlorinated aromatics [22–26]. The multiphase system consists of a substrate solution in isooctane-water (alkaline or not), a metal catalyst and a PT agent, e.g. Aliquat 336 (tricaprylmethylammonium chloride). Heated at 50 °C and

bubbled with hydrogen at atmospheric pressure, this system provides an optimal set of conditions for the reduction of polychlorinated aromatics. The presence of the aqueous base and the PT agent is sometimes indispensable for the reaction to proceed, e.g. as we have shown for the HDC of TCB with Raney-Ni [22,23]. The POPs, such as polychlorinated biphenyls (PCBs) [25] and dioxins [24] have been shown to reduce quantitatively over Pd/C under these conditions. The system, apparently too complex, affords a flexibility with which one can direct the reaction via one or another pathway by simply varying its composition, i.e. pH of the aqueous phase, the presence of the PT agent, etc.

The present study is the first example of the application of this system for the reduction of polychlorinated aliphatics. The reductive dechlorination of lindane over Pd/C, Pt/C, and Raney-Ni in the multiphase system is described. Along with the environmental issue, the effects of reaction conditions on the chemical behaviour of lindane, and some mechanistic considerations are addressed.

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}, Lot. No. H-482, composed of Ni 93% and Al 7%, having particle size distribution of 0–80 μm and surface area of 70–80 m^2/g. 5% Pd/C was from Aldrich, Art. No. 20,568-0, Lot No. 71112022. 5% Pt/C was from Fluka, Art. No. 80982, Lot No. 330334/1. Lindane was from Aldrich, γ-hexachlorocyclohexane 97%. Aliquat 336$^{®}$ (tricaprylmethylammonium chloride) was 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 6890 N GC with an HP-5MS capillary column (30 m × 0.25 mm, film thickness 0.25 μm).

The reactions were run in a 25 ml three-necked round-bottomed reactor with a water jacket, supplied with a tube for hydrogen supply, a condenser, stirred magnetically at 1000 rpm and thermostated at 50 ± 1 °C. A typical reaction was loaded with 10 ml of isooctane/toluene (1/1 (v/v)) or absolute ethanol phase, containing 0.2 g (0.7 mmol) of lindane, 0.0455 g of 5% Pd/C (0.02 mmol Pd) or 0.25 g of the Raney-Ni slurry (2 mmol Ni) or 0.0837 g of 5% Pt/C (0.02 mmol Pt), 0.059 g of n-dodecane (0.35 mmol) as the GC internal standard and, where indicated (see Tables), 0.103 g (0.26 mmol) of Aliquat 336. 5.7 ml of the aqueous KOH solution or water was added therein, if isooctane/toluene was the organic phase. If ethanol was used, KOH was dissolved in the ethanol phase, where indicated. The reaction was 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. The first one was taken
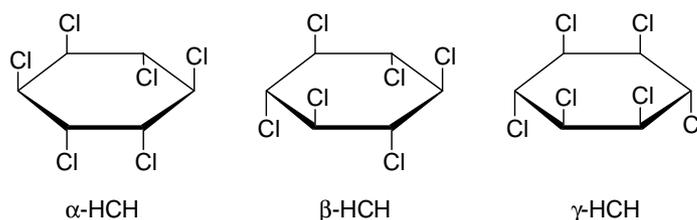
Fig. 2. α-, β-, and γ-isomers of hexachlorocyclohexane.

just after the reagents had been loaded and it was considered the zero-time point. About 20 μl of the reaction mixture was taken for each sample, which was then diluted with ethyl ether up to 1–2 ml or with ethanol if the latter was the solvent. To avoid the GC column pollution/damage and to enhance quality of analyses, the samples were shaken with silica to remove Aliquat 336, and/or filtered with glass wool to remove catalyst. The samples in ethanol, where KOH was present, were neutralized with aqueous HCl.

The quantitative analyses of the reaction mixture were performed using the GC internal standard technique, as described elsewhere [22], calibration coefficients for TCBs, dichlorobenzenes (DCBs), chlorobenzenes (CB) and benzene therein]. The coefficients for lindane and other less chlorinated cyclohexane, -ene, and -diene derivatives were assumed equal (calculated by comparing lindane and dodecane GC peak areas). Concentrations reported in tables are expressed as percentage of the initial substrate amount.

3. Results and discussion

3.1. Base-assisted dehydrochlorination of lindane

Under the multiphase catalytic conditions, i.e. in a biphasic isooctane–aqueous KOH system, containing a heterogeneous catalyst (supported Pd, Pt, or Raney-Ni) and Aliquat 336, lindane may theoretically undergo two different dechlorination processes. Either base-assisted DHC, which is catalyzed by quaternary ammonium salts [9,10]; or catalytic HDC, also possible under these conditions in the presence of hydrogen. For this second process, as we have previously shown on the examples of polychlorinated aromatics [22–26], the presences of a base and of a quaternary salt are

also necessary to achieve effective dechlorination. In order to more clearly understand the transformation pathways of lindane and how different system components affect them, we have independently analyzed these two possibilities.

In a system without metal catalyst, containing the isooctane solution of lindane and the aqueous KOH, lindane undergoes three consecutive DHC steps and is rapidly converted to a mixture of TCBs, of which the predominating product is 1,2,4-TCB (more than 90%, see Table 1). It has been reported in 1912 by Van der Linden [2] that mainly 1,2,4-TCB was obtained in the base-assisted DHC of either α-, β-, or γ-HCH isomers (Fig. 2). Cristol and coworkers in their study on the base assisted DHC of α-, β-, and γ-HCHs have pointed out that the reaction strongly depends on stereochemistry, i.e. the *trans* elimination prevails over the *cis* one [7,27].

For example, the β-isomer, having a configuration that is impossible to undergo *trans*-elimination (all chlorines are in *trans* positions to each other) reacted several orders of magnitude slower [27] than the other isomers, e.g. α-HCH, whose configuration is right for the formation of 1,2,4-TCB. It is easy to show that γ-HCH (lindane) would also yield 1,2,4-TCB, instead of 1,3,5,6-tetrachlorocyclohexa-1,4-diene (**3-A** in Fig. 3) which is not supposed to undergo *trans*-elimination.

Formation of 1,2,4-TCB in the DHC of lindane (**1**) owes to the ring inversion in the first intermediate, 1,3,4,5,6-γ-pentachlorocyclohexene, which exists in two equilibrium conformations (**2-A** and **2-B,** as shown in Fig. 3). Conformer **2-B**, which has a calculated energy 0.75 kcal/mol lower than the originally formed conformer **2-A** (a difference of the respective heats of formation by means of the ChemDraw 7.0 software using the MOPAC method), possesses a configuration favorable for elimination

Table 1
Dehydrochlorination of lindane in the isooctane–aqueous KOH system, without metal catalyst

No.	A336	KOH (%)	Time (min)	Conversion (%)	Yield (% GC)		
					PCCH[a]	DCBs	TCBs[b]
1	Yes	7	15	98	0	0	98
			70	100	0	0	100
2	Yes	50	15	100	0	5	95
3	No	7	50	70	45	0	25
			300	100	20	0	80

[a] 2,3,4,5,6-γ-Pentachlorocyclohexene.
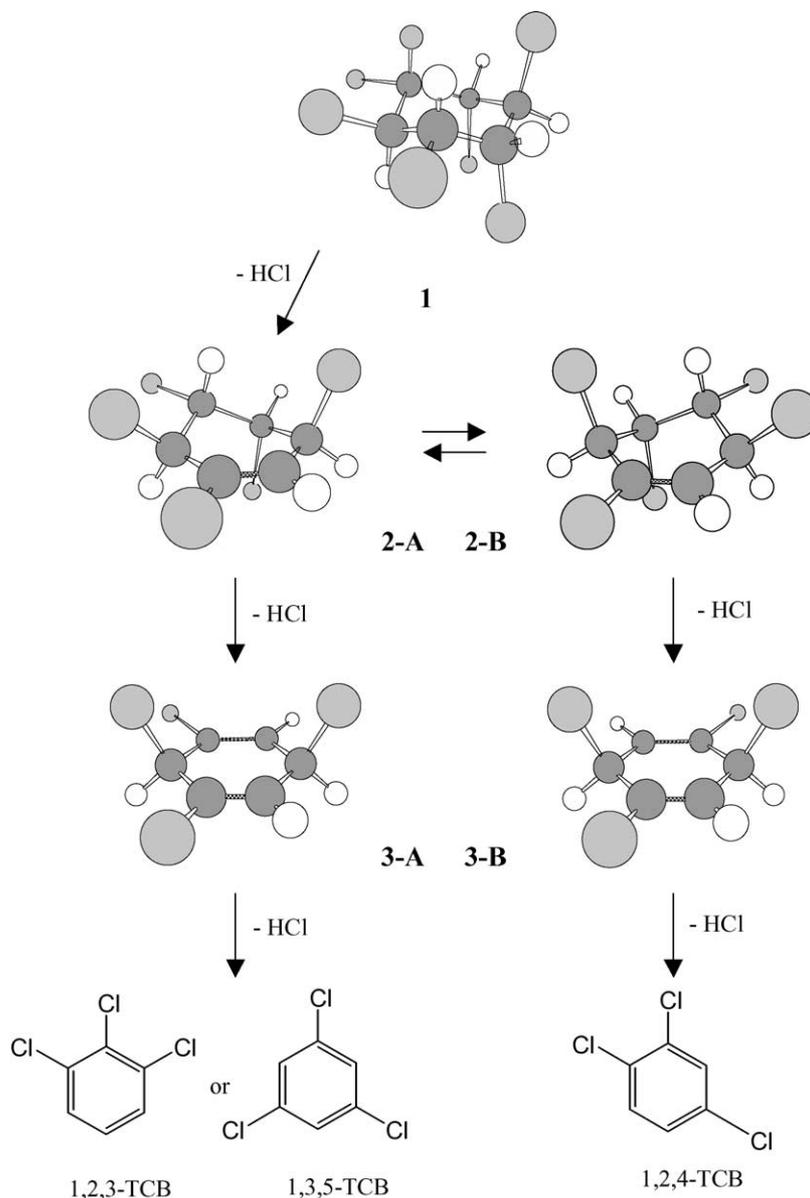[b] A sum of isomers, 1,2,4-TCB/1,2,3-TCB/1,3,5-TCB ≈ 12/1/1.

Fig. 3. Three-dimensional scheme of the hydrodechlorination pathway of lindane to 1,2,4-TCB.

of H⁺ at position 5. DHC of **2-B** gives rise to the formation of 1,3,4,6-tetrachlorocyclohexa-1,4-diene (**3-B**), instead of 1,3,5,6-tetrachlorocyclohexa-1,4-diene (**3-A**). It is easy to follow that **3-B** gives 1,2,4-TCB in the end. 1,2,3-TCB and 1,3,5-TCB, which were detected in small amounts in the final mixture (Table 1), are probably formed from **3-A**.

Concentration of KOH in the aqueous phase is not very critical for the reaction, the full conversion of lindane is reached in just 15 min if using either 7% or 50% KOH (compare entries one and two of Table 1). The HCl removal rates are high and seem to increase for subsequent steps, as witnessed by the absence of non-aromatic intermediates. However, in the experiment with 7% KOH and without Aliquat 336 (entry 3, Table 1) formation of intermediate 1,3,4,5,6-γ-pentachlorocyclohexene (**2-A** or **2-B** in Fig. 3,

or **8** in Fig. 4), as confirmed by GC–MS, was observed in the beginning of the reaction (45% yield in 25 min). The reaction without PT agent is also considerably slower (compare entries one and three of Table 1). The substrate disappeared in only 300 min, though with only 80% yield of TCBs (**2** in Fig. 4), while the residual 20% was still **8** (Fig. 4).

3.2. Dehydrochlorination versus catalytic hydrodechlorination of lindane under multiphase conditions

In the isooctane–aqueous KOH system, containing the PT agent (Aliquat 336), a heterogeneous metal catalyst (supported Pd/C, Pt/C, or Raney-Ni), and bubbled with hydrogen (Table 2), the reaction of lindane follows the **1** (→ **2**) → **3** → **4** → **5** pathway (Fig. 4), with the first step being the
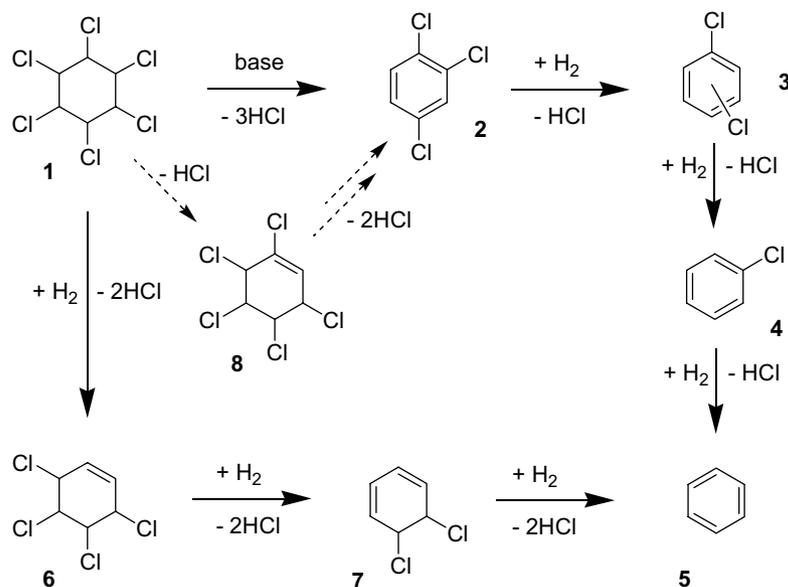
Fig. 4. Catalytic reduction of lindane to benzene via two diverse pathways and the corresponding intermediates (major ones observed by GC–MS are shown).

base assisted elimination reaction to TCBs (1,2,4-isomer). The DHC selectively precedes the catalytic HDC of TCBs to benzene, the former being much faster than the latter. No products arising from the HDC/hydrogenation of the starting material or from the intermediates formed before TCBs were detected (e.g. cyclohexane or its chlorinated derivatives).

The reduction of TCBs proceeds mainly to the *o*-isomer of DCB (80–90%), which then gives CB, and benzene, as the final product. The reaction of TCBs to benzene over either Pd/C or Raney-Ni proceeds rapidly, with no sign of inhibition (entries one and two of Table 2). This is in accordance with the data obtained previously for the HDC of polychlorinated benzenes over Pd/C and Raney-Ni under similar conditions [21,23]. As we have also reported previously [24], Pt/C is poorly active in the HDC of chlorinated aromatics under these conditions; also in this case (entry

three) the reduction of TCB on Pt/C appeared quite slow and did not reach complete conversion due to a notable rate inhibition.

The reaction on Pt/C stops at nearly 60% yield of DCBs, whereas CB and residual TCBs are present in far smaller amounts. This suggests that the HDC rate for TCB on Pt/C is lower than that for DCB. On the contrary, the rates for consecutive HDC steps on Raney-Ni grow with decreasing the number of chlorines; DCBs were found in small quantities, and CB was practically not present through the reaction course up to benzene. With Pd/C the HDC rates for TCBs, DCBs, and CB seem to be comparable since all these intermediates are present in high and comparable concentrations throughout the reaction. These data are also in agreement with those obtained previously for the HDC or chlorinated benzenes over these catalysts [22,24,28].

Table 2
Reaction of lindane with H_2 over metal catalysts in the isooctane–7% aqueous KOH system in the presence of Aliquat 336

No.	Catalyst	Time (min)	Conversion (%)	Yield (% GC)				
				PCCH[a]	TCBs[b]	DCBs[c]	CB	PhH[d]
1	5% Pd/C	7	93	2	35	25	25	– (6)
		22	100	0	26	20	6	– (48)
		190		0	0	3	6	– (91)
2	Raney-Ni	5	100	0	94	4	0	2 (2)
		90		0	1	3	0	70 (96)
3	5% Pt/C	5	100	0	75	19	2	– (4)
		250		0	10	65	12	– (13)

[a] 2,3,4,5,6-γ-Pentachlorocyclohexene.
[b] A sum of isomers, 1,2,4-TCB/1,2,3-TCB/1,3,5-TCB ≈ 8/1/1.
[c] A sum of isomers, *o*-/*m*-/*p*- ≈ 5/1/1.
[d] Not determined or with a big error due to a rapid evaporation from the reaction mixture, numbers in brackets indicate the calculated corrected content.

Table 3
Reaction of lindane with H_2 over metal catalysts in the isooctane–aqueous (non-basic) system in the presence of Aliquat 336

No.	Catalyst	Aqueous phase	Time (min)	Conversion (%)	Yield (% GC)					
					CB	PCCH[a]	BTC[b]	BDC[c]	others[d]	PhH[e]
1	5% Pd/C	Water	50	100	1	1/0	0	0	1	52 (97)
			280		0	0	0	0	0	8 (100)
2	5% Pt/C	Water	30	40	0	1/4	0	0	0	11 (35)
			270	99	0	1/0	0	0	1	– (97)
3	Raney-Ni	Water	10	93	7	0/2	25	12	6	34 (41)
			20	100	8	0	0	0	7	58 (85)
4	5% Pd/C	HCl, 1.16 M	100	90	0	0	0	0	0	47 (90)
			300	100	0	0	0	0	0	30 (100)

[a] 1,2,3,4,5-γ-Pentachlorocylohexane/2,3,4,5,6-γ-pentachlorocyclohex-1-ene.
[b] Benzene tetrachloride (3,4,5,6-tetrachlorocyclohex-1-ene).
[c] Benzene dichloride (5,6-dichlorocyclohexa-1,3-diene).
[d] DCBs, chloro- and dichlorocyclohexane.
[e] Not determined or with a big error due to a rapid evaporation from the reaction mixture, numbers in brackets indicate the corrected content.

3.3. Reductive dechlorination of lindane over Raney-Ni, Pd/C, and Pt/C in the absence of base

The reaction profiles change dramatically if running the reaction of lindane over Raney-Ni, Pd/C or Pt/C in the absence of base (pure water as the aqueous phase), with or without Aliquat 336 (Table 3). Similarly, the final major reaction product was benzene, but was apparently formed via a different pathway, since TCBs were not detected at all during the reaction. The reaction on Pd/C and Raney-Ni in the presence of Aliquat 336 was completed within 1 h (entries one and three) with the yields of benzene of 97% (Pd/C) and 85% (Raney-Ni). On Pt/C, the 97% conversion to benzene was reached in 270 min (entry two). The reaction on Pd/C proceeds in a similar manner also if using an aqueous acid solution instead of water, but with a significantly lower rate (entry four).

The respective reactions of lindane on Pd/C or Raney-Ni in ethanol (entries one and two, Table 4) proceeded with the same selectivity and via the same intermediates as in the isooctane-water system with Aliquat 336, but was very slow. Only 29% conversion was attained on Pd/C in 3 h; on Raney-Ni the reaction, though faster, stopped at 88% conversion. With KOH dissolved in ethanol the reaction

on Raney-Ni proceeds via the DHC–HDC pathway (entry three, Table 4), similarly to the multiphase basic system (see Table 2). However, the HDC rate in such a system was far slower than in the multiphase one. Chlorinated benzenes were present in the substantial quantities even after 250 min reaction time (entry three, Table 4).

One of the advantages of this alternative pathway is a higher rate of benzene formation, even though the complete disappearance of lindane is attained more rapidly in the system with KOH. Comparing the reactions with and without KOH (Tables 2 and 3) one can note that in the system without KOH the full conversion to benzene is attained in a shorter time, because the intermediate TCBs are reduced quite slowly.

3.4. Mechanism of lindane dechlorination over metal catalysts without base

Previously we have shown that the HDC of 1,3,5- or 1,2,4-TCBs is very sluggish over Pd/C [26] in the absence of base or even does not proceed at all over Raney-Ni [22]. The HDC of TCBs on Pt/C is inhibited even in the presence of base, as was also pointed out above. Therefore, the absence of TCBs in the reaction is not likely

Table 4
Reaction of lindane with H_2 over 5% Pd/C and Raney-Ni in ethanol

No.	Catalyst	KOH (%)	Time (min)	Conversion (%)	Yield (% GC)					
					BTC	BDC	TCBs	DCBs	CB	PhH[a]
1	5% Pd/C	No	180	29	0	0	0	0	0	6 (29)
2	Raney-Ni	No	5	10	2	5	0	0	0	– (3)
			90	88	23	2	0	0	19	– (44)
			165	88	19	1	0	0	10	– (58)
3	Raney-Ni	15	2	98	0	0	90[b]	3[b]	3	2
			250	100	0	0	4[c]	19[c]	8	6 (69)

[a] Not determined or with a big error due to a rapid evaporation from the reaction mixture, numbers in brackets indicate the corrected content.
[b] A sum of isomers, 1,2,4-TCB/1,3,5-TCB/1,2,3-TCB ≈ 20/2/1.
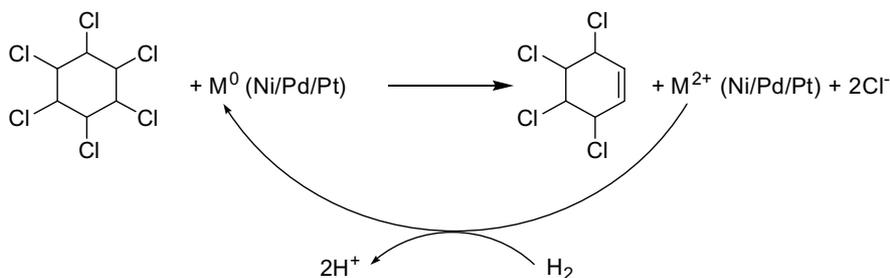[c] A sum of isomers, o-/m-/p- ≈ 3/3/1.

Fig. 5. Removal of a pair of chlorines from lindane via the catalytic reaction with hydrogen over Raney-Ni, Pd/C or Pt/C in the absence of base.

a result of their rapid subsequent reduction, but is an evidence of another reaction pathway. In fact, in the experiment with Raney-Ni the dominating intermediates were BTC (3,4,5,6-tetrachlorocyclohex-1-ene) and BDC (5,6-dichlorocyclohexa-1,3-diene), as confirmed by GC–MS (Tables 3 and 4), however, these were not detected in the reactions on Pd/C or Pt/C.

DCBs, CB, mono- and dichlorocyclohexane were also formed in small amounts as intermediates or remained unreacted. Cyclohexane was probably another by-product, but was not formed in sensible amounts (technically, its formation in low concentrations could not be followed by GC). Obviously, DCBs and CB in this case were not formed from TCB; otherwise, the latter would have been present as an intermediate since it reduces less readily than DCBs or CB under these conditions. The chlorinated cyclohexanes were also not likely to be formed from the respective chlorobenzenes, as the reduction of aromatic ring does not occur over Pd/C and Raney-Ni under the conditions given. Therefore, the presence of small amounts of CB, DCBs, and mono- and dichlorocyclohexane owes rather to a lateral reduction of key intermediates **6** and **7**, e.g. via a conjunction of side processes of their HDC, DHC, and double bond hydrogenation.

The presence of BTC (**6**) and BDC (**7**) in the reaction on Raney-Ni suggests that the reduction of lindane to benzene in the absence of base proceeds via the $1 \to 6 \to 7 \to 5$ pathway, i.e. with formation of the aromatic ring at the final stage (see Fig. 4). This proposes a general mechanism, according to which the chlorines are removed in pairs from adjacent positions.

Theoretically, the removal of a pair of chlorines with formation of a double bond could be a consecutive process involving DHC and HDC steps, however, we suppose that this is not likely to occur, since DHC is not possible or is too sluggish without base. Only traces of pentachlorocyclohexane and pentachlorocyclohexene intermediates were observed, which indeed may have been formed via some contribution of the DHC and HDC reactions of the substrate, but the less chlorinated non-saturated products, indicative of these reactions, were not detected in the in the reactions over Pd/C or Pt/C.

We suppose, that either on Raney-Ni or Pt or Pd on carbon the removal of a pair of chlorines takes place via

a redox reaction of lindane with the zerovalent metal, as shown in Fig. 5. This is also in agreement with the results reported by Beland et al. [11] for electrochemical and anaerobic processes of lindane dechlorination to benzene, where only γ-BTC was observed as intermediate, i.e. the loss of adjacent chlorines occurred. The mechanism, involving the removal of vicinal chlorines and the resulting formation of a double bond, is usually proposed to take place also in the hydrodechlorination of di- and more chlorinated alkanes over Pd/C in the gas-phase [29,30].

Interestingly, the intermediates BTC and BDC were formed only in the reaction over Raney-Ni, but were not observed in the reactions over Pd/C or Pt/C. An explanation might be that either the rates of the steps, following the removal of the first two chlorines, increase substantially on Pt and Pd on carbon, or that the removal of six chlorines takes place concertedly on Pt and Pd, or be indicative of a stronger adsorption of the reaction intermediates that react before being desorbed to the bulk phase.

In the experiments with Raney-Ni, the excess of the latter with respect to the substrate was normally used (2 mmol Ni versus 0.7 mmol substrate), because of a considerably lower surface area and a lower activity of Raney-Ni with respect to Pt or Pd on carbon. Nevertheless, we consider this reaction catalytic, i.e. not simply a red-ox reaction with a stoichiometric amount of Ni. This was confirmed by running an experiment using Raney-Ni in ethanol without hydrogen. Only 15% conversion of lindane to BTC had place before the reaction stopped, implying that the presence of hydrogen is necessary for the reaction to proceed. In the presence of a seven-fold bigger amount of Raney-Ni (14 mmol) the conversion increased proportionally (i.e. 95%, Fig. 6).

The possibility of lindane reaction by residual Al (7% in the Raney-Ni sample), or by hydrogen adsorbed on Raney-Ni in the abovementioned experiment can be discarded. This was proven by running an experiment with chlorobenzene (0.7 mmol) using also the excess of Raney-Ni (10 mmol), in the absence of hydrogen. The experiment with chlorobenzene was carried out in isooctane in the presence of the aqueous base (the latter could also provoke formation of hydrogen from Al) and Aliquat 336; under such conditions, in the presence of hydrogen, chlorobenzene is reduced within several minutes. Instead, in the absence of
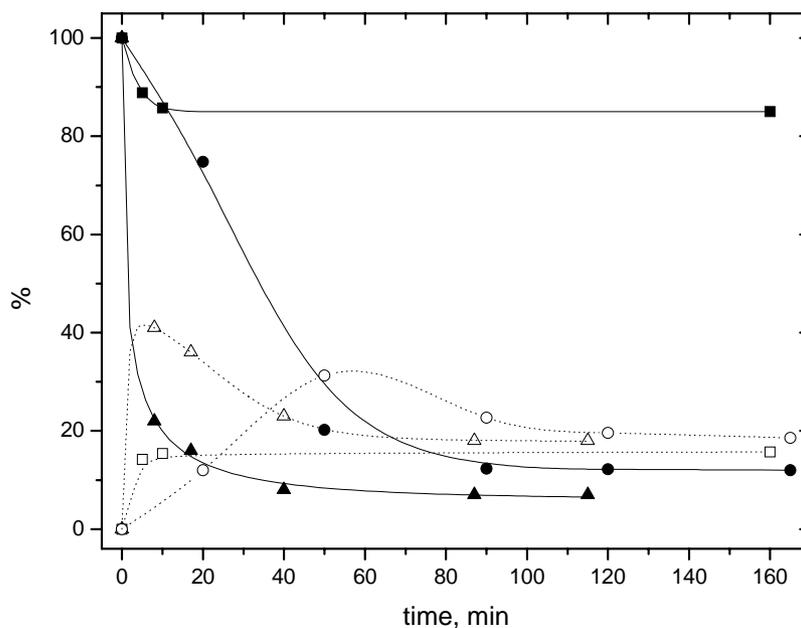
Fig. 6. Disappearance of lindane (lines and solid symbols) and formation of BTC (dots and hollow symbols) over Raney-Ni in ethanol in the reactions 1) with hydrogen, 2 mmol Ni (see also entry 2, Table 4) (●, ○); (2) without hydrogen, 2 mmol Ni (■, □); (3) without hydrogen, 14 mmol Ni: (▲, △). Other products (CB and benzene) are not shown.

hydrogen, no reaction occurred within 1 h, even though the molar Ni–Cl ratio in this case was higher than in the experiment with lindane. This leads to the conclusion that the amount of hydrogen or Al present originally on Raney-Ni is insufficient to promote dechlorination, and therefore the reaction indeed takes place between lindane and metallic Ni, as proposed in the mechanistic scheme (Fig. 5).

The same reaction of lindane over Raney-Ni in ethanol with hydrogen (entry two, Table 4) proceeded up to nearly 90% conversion but then was also inhibited (see also Fig. 6). The inhibition is probably due to the buildup of HCl, which contributes to the competitive oxidation of Ni, and, therefore, deactivates it. Under the multiphase conditions, HCl could transfer to the aqueous phase that would prevent this deactivation. We have noted in addition, that also under the multiphase conditions the presence of acid in the aqueous phase slows down the reaction on Pd/C (entry four of Table 3).

3.5. Role of Aliquat 366 as a promoter

We have reported on the rate acceleration by Aliquat 336 and other PT agents (quaternary ammonium salts) in the HDC of various chlorinated aromatics in the multiphase isooctane-aqueous KOH system with Pd/C and Raney-Ni [22–26]. We have proposed that the effect of Aliquat 336 is linked to its adsorption on the catalyst surface and formation of a nano-layer, which creates an ionic-liquid environment favorable for the reaction [22,31]. This liquid film may, among other effects, preserve the catalyst surface from poisoning by HCl [32,33].

It should be noted that in the present case, the co-catalytic effect of Aliquat 336 was observed in a non-basic system. The reaction of lindane on Pd/C under multiphase conditions was speeded up nearly tenfold with Aliquat 336 (see Fig. 7), but the composition of intermediates/products was not affected. In the reaction over Pd/C in EtOH, the presence of Aliquat 336, however, had little or no effect on the reaction, which in either case proceeded very slow (Fig. 7). Previously, we have shown that the presence of Aliquat 336 in the HDC reactions in EtOH does not create any difference [22], because Aliquat 336 is well soluble in EtOH and it is less likely to have so much surface affinity like in isooctane, where it is more sparingly soluble. However, for the same reaction in pure isooctane (without water) the effect of Aliquat 336 is absent (Fig. 7). Therefore, the role of Aliquat 336 in the reaction of lindane under multiphase conditions without base must be linked to the presence of water.

From all evidence, the role of Aliquat 336 in the reduction of lindane under multiphase conditions might be connected to a formation of a separate liquid layer by Aliquat 336, which holds inside the catalyst particles and brings them close to the liquid-liquid interface. In this connection, the presence of water might owe its importance to an effect of a reservoir for HCl. Aliquat 336, embracing the metal catalyst and situated at the interface, helps to transfer HCl to the aqueous phase, therefore preventing catalyst deactivation by HCl. In fact, a combined presence of water and Aliquat 336 is required, as was discussed above (Fig. 7). This hypothesis is in accordance with our previous results [29], where it has been shown that a liquid layer is visually
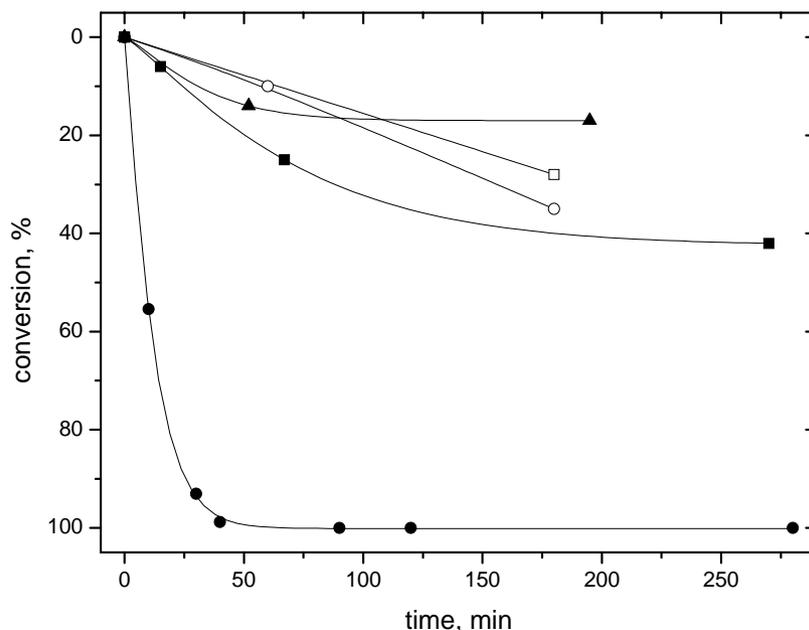
Fig. 7. Effect of Aliquat 336 on the rate of lindane dechlorination with hydrogen over Pd/C in the absence of base. Reactions with (solid symbols) and without (hollow symbols) Aliquat 336 in the isooctane-water system (●, ○), in ethanol (■, □), and in isooctane (no aqueous phase) (▲).

recognized between water and organic phases in the mixture of isooctane, water, and Aliquat 336. Since Aliquat 336 per se is partly soluble in pure isooctane (at least up to 10% (v/v)), the observed third layer of Aliquat 336 must contain water in order to phase-separate. When KOH is present, the third layer was not formed, implying that A336 is dissolved in the organic phase.

4. Conclusions

We have demonstrated that the reductive dechlorination of lindane in the multiphase isooctane-aqueous system over Pd/C and Raney-Ni with hydrogen can be selectively carried out to benzene in short times (within 1 h) and at 50 °C and atmospheric pressure. The composition of the multiphase system, e.g. the presence of aqueous KOH or water and that of a quaternary ammonium salt (Aliquat 336) were shown to be very critical factors.

Reduction of lindane in the presence of base, a metal catalyst, and hydrogen was shown to proceed via the consecutive DHC–HDC reaction stages, which are both co-promoted by Aliquat 336 and aqueous KOH. The DHC of lindane under basic conditions was shown to afford selectively TCBs, which then undergoes the HDC to benzene. 1,2,4-Isomer is formed predominantly (90% or more of overall TCBs), because of the ring inversion in the first DHC intermediate to a more favorable configuration, as confirmed by molecular calculations.

It has been also established that the reaction of lindane to benzene with hydrogen under the multiphase conditions or in ethanol, but in the absence of base, proceeds via a dif-

ferent pathway, involving consecutive steps of the reductive elimination of a pair of adjacent chlorines with formation of a double bond. The results obtained for the reaction with Raney-Ni suggest that the removal of a pair of chlorines occurs via a red-ox reaction of lindane and the zerovalent metal, which is subsequently reduced with hydrogen. The reaction is assumed to proceed in the same fashion over Pd/C and Pt/C, as well.

The presence of Aliquat 336 was found to result in a substantial increase of the reaction rate in this process, but only in the biphasic system with water. Presumably, the role of Aliquat 336 is connected to formation by the latter of a separate liquid phase located at the isooctane-water interface, which embraces the metal catalyst and prevents its deactivation by simplifying the transfer of HCl released in the reaction to the aqueous phase. The reactions where no water was present or with already acidic aqueous phase proceeded with slower rates and/or were subject to inhibition.

The dechlorination of lindane in the non-base system may appear more attractive from both synthetic and environmental aspects. As concerns the detoxification issue, formation of TCBs as intermediates in the well-studied processes of HDC of lindane or its isomers poses a risk of formation of even more toxic substances, such as polychlorinated phenols and dioxins, e.g. upon a circumstantial overheating of the mixture. An advantage of the reaction under the multiphase conditions without base may be drawn from its alkene and diene intermediates, the former being precious reagents for synthetic applications. On the other hand, the way of lindane utilization to benzene via the DHC to TCB versus the HDC of the latter can also benefit from the use of the multiphase conditions, since the abovementioned processes are

both promoted by Aliquat 336 and the aqueous base and, therefore, can be carried out one pot.

In conclusion, we believe that the multiphase methodology can find a valuable application in the utilization of lindane and its wastes, as we have already demonstrated for other pollutants of the kind, containing aromatic chlorines.

Acknowledgements

References

[1] See for example the web sites of the Agency for Toxic Substances and Disease Registry (ATSDR, www.atsdr.cdc.gov), and of the EPA (http://www.epa.gov).
[2] Van der Linden, Chem. Ber. 45 (1912) 236.
[3] K. Breivik, J.M. Pacyna, J. Münch, Sci. Total Environ. 239 (1999) 151.
[4] K.S. Schafer, Going, Going, Gone? Lindane Moves Closer to Elimination, Environmental Media Services, http://www.ems.org/pops/lindane.html.
[5] J. Vikelsoe, E. Johansen, Chemosphere 40 (2000) 165.
[6] N. Zinin, Zeitschrift fuer Chemie (1871) 284.
[7] S.J. Cristol, J. Am. Chem. Soc. 69 (1947) 338.
[8] B. Ngabe, T.F. Bidleman, R.L. Falconer, Environ. Sci. Technol. 27 (1993) 1930.
[9] F.S. Sirovski, E.R. Berlin, S.A. Mulyashov, E.A. Bobrova, Z.I. Batrakova, D.F. Dankovskaya, Org. Process Res. Dev. 1 (1997) 253.
[10] F.S. Sirovski, Org. Process Res. Dev. 3 (1999) 437.
[11] F.A. Beland, S.O. Farwell, A.E. Robocker, R.D. Geer, J. Agric. Food. Chem. 24 (1976) 753.
[12] P.J.M. Middeldorp, M. Jaspers, A.J.B. Zehnder, G. Schraa, Environ. Sci. Technol. 30 (1996) 2345.
[13] B.C. Okeke, T. Siddique, M.C. Arbestain, W.T. Frankenberger, J. Agric. Food Chem. 50 (2002) 2548.
[14] W.J. Catallo, T. Junk, Waste Manage. 15 (1995) 303.
[15] B.J. Mincher, D.H. Meikrantz, R.J. Murphy, G.L. Gresham, M.J. Connolly, Int. J. Rad. Appl. Instrum. A 42 (1991) 1061.
[16] A. Kubátová, A.J.M. Lagadec, S.B. Hawthorne, Environ. Sci. Technol. 36 (2002) 1337.
[17] C. Schüth, M. Reinhard, Appl. Cat. B 18 (1998) 215.
[18] A. Perosa, P. Tundo, M. Selva, J. Mol. Catal. A 180 (2002) 169.
[19] A. Perosa, P. Tundo, S. Zinovyev, Green Chem. 4 (2002) 492.
[20] A. Bomben, C.A. Marques, M. Selva, P. Tundo, Synthesis (1996) 1109.
[21] P. Tundo, S. Zinovyev, A. Perosa, J. Catal. 196 (2000) 330.
[22] S. Zinovyev, A. Perosa, S. Yufit, P. Tundo, J. Catal. 211 (2002) 347.
[23] C.A. Marques, O. Rogozhnikova, M. Selva, P. Tundo, J. Mol. Catal. A 96 (1995) 301.
[24] A. Perosa, M. Selva, P. Tundo, S.S. Zinovyev, Appl. Catal. B 32 (2001) L1.
[25] C.A. Marques, M. Selva, P. Tundo, J. Org. Chem. 59 (1994) 3830.
[26] C.A. Marques, M. Selva, P. Tundo, J. Org. Chem. 58 (1993) 5256.
[27] S.J. Cristol, N.L. Hause, J.S. Meek, J. Am. Chem. Soc. 73 (1951) 674.
[28] S.S. Zinovyev, Ph.D. thesis, N.D. Zelinsky Institute of Organic Chemistry, Moscow, 2002.
[29] V.V. Lunin, E.S. Lokteva, Izv. Acad. Nauk. Ser. Khim. (Russ. Chem. Bull.) (1996) 1609 (in Russian), and references therein.
[30] G. Centi, J. Mol. Cat. A 173 (2001) 287.
[31] P. Tundo, A. Perosa, S.S. Zinovyev, J. Mol. Catal., in press.
[32] J.B. Hoke, G.A. Gramiccioni, N.L. Balko, Appl. Catal. B 1 (1992) 285.
[33] P. Pasett, F. Gentile, J. Org. Chem. 60 (1995) 1351.