

## Selectivity in hydrodehalogenation of polychloro- and polybromobenzenes under multiphase conditions

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### Abstract

The competitive hydrodehalogenation of isomeric *o*-, *m*- and *p*-dichloro (and dibromo) benzenes with H<sub>2</sub> at atmospheric pressure and Pd/C or Ni–Raney carried out in a multiphase system (organic solvent and 50% KOH aq. solution) is influenced by the presence of a bulky quaternary onium salt where both the catalytic activity and the selectivity change in relation to the halogen to be removed and the metal catalyst used. In particular, the Ni–Raney catalyst becomes effective in the reduction only if an onium salt is added. Similarly, the onium salt effects the catalytic hydrodehalogenation of 1,2,4-trichloro- and 1,2,4-tribromobenzene.

**Keywords:** Carbon; Hydrodehalogenation; Multiphase system; Ni–Raney; Onium salt; Palladium; Pd/C Selectivity

### 1. Introduction

Hydrodehalogenation reactions compared to other detoxification methods [1,2] are gaining importance because they allow the polyhalogenated aromatics to be reduced to the parent hydrocarbons without the production of waste. Moreover they may selectively remove the halogen from the aromatic ring, thus providing new methods for organic synthesis [3,4].

We previously reported [5] that in the dehalogenations of aromatics catalyzed by palladium on carbon (Pd/C) with hydrogen at atmospheric pressure in a two-phase system (aqueous KOH and organic solvent), the presence of an onium salt as a phase-transfer (PT) catalyst could change both the catalytic activity and the selectivity in the

removal of the halides from different positions of the aromatic ring. For example, these reaction conditions allowed a very rapid hydrodechlorination on sterically hindered compounds (i.e., 2-chloro-*m*-xylene and PCBs) [5]. In addition, in the presence of Aliquat 336 (tricaprylmethylammonium chloride, **1**) an unusual selectivity occurred in the reduction of isomeric dichlorobenzenes carried out in diethyl ether at 20°C: the *o*-isomer reacted 5.3 times faster than the *p*-one.

We wish to report here that by varying the metallic catalyst under multiphase conditions, the onium salt considerably induces different reaction outcomes in the dehalogenation of polychloro- and polybromobenzenes as well.

In particular, the catalytic activity and the selectivity of both Pd/C and Ni–Raney are considered. At first, the reduction of *o*-, *m*- and *p*-dichloro and dibromobenzene isomers are reported and then the

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trichloro- and tribromobenzene derivatives are studied.

The selectivity in the removal of different halogens bonded to the same aromatic ring is also discussed through the investigation of the reduction of 1-bromo-4-chloro-, 1-bromo-2,6-dichloro-, and 1-bromo-3-fluoro-4-iodobenzene.

## 2. Experimental

### 2.1. General

All reagents and solvents were commercially available and were used without further purification. 5% Pd/C and Ni–Al alloy were Fluka, Arts. Nos. 75992 and 72240, respectively.

The metallic catalysts (Pd/C or Ni–Raney) was used according to the following molar ratios: (i) Pd/Cl and Pd/Br in the range of 0.0051–0.01; (ii) Ni/Cl and Ni/Br in the range of 0.68–1.36.

The mixtures were magnetically stirred at 1000 rpm in a 25 ml three-necked round-bottomed thermostated flask, connected with a system for the addition of hydrogen. The reactions courses were followed by gas chromatography: comparison with authentic samples were done. The conversions were referred to the internal standard (*n*-decane).

GC analyses were performed on a Varian GC 3400 using a fused silica capillary column (30 m × 0.25 mm) with DB-5 as the liquid phase (film thickness 0.25 mm) and with a FID detector.

### 2.2. Preparation of the Ni catalyst

The Ni–Raney catalyst was prepared in situ as described in literature [6]: Ni–Al powder (0.235 g, 2.0 mmol Ni) was added to KOHaq. (50%, 4 ml) at 50 or 20°C and magnetically stirred for about 40 min until the evolution of H<sub>2</sub> ceased. Then, in the same vessel, the reaction was started: the reagent solution and Aliquat 336 were added and H<sub>2</sub> was bubbled at atmospheric pressure in the organic phase at about 1 ml/min.

### 2.3. Reduction procedures

#### 2.3.1. Competitive hydrodehalogenation reactions of isomeric dichloro- and dibromobenzenes with Pd/C or Ni–Raney catalyst – (Table 1)

A mixture of KOH(aq.) (50%, 4 ml), 7.0 ml of organic solution (isooctane or *n*-pentane) of *o*-, *m*- and *p*-dichlorobenzenes or dibromobenzenes (each at 0.07 M; 1.47 mmol in total), the catalyst (5% Pd/C: 0.032 g, 0.015 mmol; Ni–Raney: 0.235 g, 2.0 mmol) and Aliquat 336 (0.085 g, 0.20 mmol) was loaded into a 25 ml three-necked round-bottomed flask and magnetically stirred at 1000 rpm. The flask was thermostated at 50 or 20 ± 0.1°C and connected with a system for the inlet of H<sub>2</sub>; the latter was bubbled at atmospheric pressure in the organic phase at about 1 ml/min. *n*-Decane was used as the internal standard.

#### 2.3.2. General procedure for hydrodehalogenation of aryl halides with Pd/C or Ni–Raney catalysts – (Tables 2–6)

An organic solution (0.07 M) of each substrate (1,2,4-trichloro- and tribromobenzenes, 1-bromo-4-chlorobenzene, 1-bromo-2,6-dichlorobenzene and 1-bromo-3-fluoro-4-iodobenzene) was prepared and *n*-decane was used as the internal standard.

A mixture of KOH(aq.) (50%, 4 ml), an organic solution of the substrate (7 ml, 0.49 mmol), the catalyst (5% Pd/C: 0.032 g, 0.015 mmol; Ni–Raney: 0.245 g, 0.20 mmol) and Aliquat 336 (0.085 g, 0.20 mmol) was loaded into a 25 ml three-necked round-bottomed flask and magnetically stirred at 1000 rpm. The flask was thermostated at 50 or 20 ± 0.1°C and connected with a system for the inlet of H<sub>2</sub>; the latter was bubbled at atmospheric pressure in the organic phase at about 1 ml/min. *n*-Decane was used as the internal standard.

### 3. Results and discussion

#### 3.1. Hydrodehalogenation of *o*-, *m*- and *p*-dichloro and dibromobenzene isomers

The competitive hydrodehalogenation of the dichloro- and dibromobenzenes (DCBs and DBBs, respectively) was investigated first. When the three isomers (*o*-, *m*- and *p*-) are simultaneously reacted, a unique intermediate (chlorobenzene or bromobenzene) and a single final product (benzene) originate so that the kinetic constant for each compound can be easily determined. In fact, correct pseudo zero-order constants are obtained for each the three isomers (for both the dichlorobenzenes or the dibromo- ones). The results are reported in Table 1.

For simplicity, only the kinetic constant for the *ortho*-isomer is reported ( $k_{ortho}$ ) and the ratios  $k_{meta}/k_{ortho}$  and  $k_{para}/k_{ortho}$  are shown; that is, in entry 1 of Table 1,  $k_{meta} = k_{ortho} \times 1.04 = 66$  M/s and  $k_{para} = k_{ortho} \times 0.71 = 45$  M/s. The time

required for the dichlorobenzene mixture to be reduced to benzene is also reported.

In the hydrodehalogenation of the *o*-, *m*- and *p*-dichloro and dibromobenzene isomers, Pd/C allows a faster reaction than Ni–Raney both at 50°C in isooctane and at 20°C in *n*-pentane (compare entries 1–4 and 9–12 with 5–8 and 13–14, respectively). However, depending on the metal catalyst used, the presence of the onium salt has a remarkable effect. Particularly in the case of Pd/C, when Aliquat 336 is used, a decrease in the reaction rate is observed (more evident at low temperatures with the dibromobenzenes; entries 11 and 12).

By contrast, the Ni–Raney catalyst expressly needs the presence of the PT agent for the reduction to occur; otherwise, no reaction takes place (entries 6 and 8).

As we previously reported [5], under our multiphase conditions the PT agent coats the metal catalyst surface, so that it might intervene by modifying the adsorption process of the halogenated

Table 1  
Competitive hydrodehalogenation of *o*-, *m*- and *p*-dichloro- and dibromobenzenes under multiphase conditions<sup>a</sup>

Entry	Substrate	Catalyst <sup>b</sup>	Solvent	PT agent <sup>c</sup>	$k_{ortho} \times 10^4$ (M s <sup>-1</sup> ) <sup>d</sup>	( $k_{ortho}:k_{meta}:k_{para}$ ) <sup>e</sup>	<i>t</i> (min)	% Benzene
1 <sup>f</sup>	DCBs	Pd/C	Isooctane	1	63.0	1.00:1.04:0.71	60	100
2 <sup>f</sup>	DCBs		Isooctane	no	97.0	1.00:1.03:1.01	50	99
3 <sup>f</sup>	DCBs		<i>n</i> -Pentane	1	6.7	1.00:1.05:0.44	130	99
4 <sup>f</sup>	DCBs		<i>n</i> -Pentane	no	7.0	1.00:0.93:0.99	110	92
5	DCBs	Ni–Raney	Isooctane	1	4.0	1.00:0.83:0.64	150	97
6	DCBs		Isooctane	no	–	–	180	–
7	DCBs		<i>n</i> -Pentane	1	0.6	1.00:0.95:0.60	370	95
8	DCBs		<i>n</i> -Pentane	no	–	– <sup>g</sup>	180	–
9	DBBs	Pd/C	Isooctane	1	4.4	1.00:1.42:1.50	135	100
10	DBBs		Isooctane	no	16.0	1.00:1.21:1.50	50	100
11	DBBs		<i>n</i> -Pentane	1	0.7	1.00:2.00:2.02	360	70
12	DBBs		<i>n</i> -Pentane	no	12.5	1.00:1.11:1.08	75	100
13	DBBs	Ni–Raney	Isooctane	1	12.0	1.00:0.79:0.53	80	100
14	DBBs		<i>n</i> -Pentane	1	2.5	1.00:0.97:0.22	250	96

<sup>a</sup> The reactions were carried out at 50°C in isooctane and 20°C in *n*-pentane and Et<sub>2</sub>O. For details, see Experimental. *o*-, *m*- and *p*-dichlorobenzenes: 0.21 M (0.07 M of each).

<sup>b</sup> Pd: 0.015 mmol and Ni: 2.0 mmol.

<sup>c</sup> 1: Aliquat 336.

<sup>d</sup> Zero-order reaction rates for *ortho*-dichlorobenzene.

<sup>e</sup> Normalized ratios between corresponding rate constants for *o*-, *m*- and *p*-isomers, respectively ( $k_{ortho}$  is set equal to unity).

<sup>f</sup> From [5]

<sup>g</sup> No reduction after 180 min.

Table 2  
Catalytic hydrodehalogenation of 1,2,4-trichlorobenzene under multiphase conditions <sup>a</sup>

Entry	Catalyst <sup>b</sup>	Solvent	PT agent <sup>c</sup>	T (°C)	t (min)	Conv. (%)	Yields (%)				
							Dichlorobenzenes <sup>d</sup>			PhCl	PhH
							<i>ortho</i> -	<i>meta</i> -	<i>para</i> -		
1	Pd/C	Isooctane	1	50	30 (35)	96 (100)	6.0 (2.0)	2.5 (-)	1.5 (-)	3.0 (1.0)	83 (97)
2		Isooctane	no	50	20	100	7.0	2.0	1.0	9.0	81
3		Diethyl ether	1	20	60	100	4.0	1.5	2.0	3.5	89
4		Diethyl ether	no	20	30	100	20.0	6.0	4.0	15.0	55 <sup>e</sup>
5	Ni-Raney	Isooctane	1	50	150	100	26.0	15.0	11.0	38.0	10 <sup>f</sup>
6		Isooctane	no	50	180	0	-	-	-	-	- <sup>g</sup>
7		Diethyl ether	1	20	360	79	32.0	18.0	11.0	11.0	7
8		Diethyl ether	no	20	180	0	-	-	-	-	- <sup>g</sup>

<sup>a</sup> For reaction conditions see Experimental. TCB: 0.07 M (0.49 mmol).

<sup>b</sup> Pd/C: 0.015 mmol and Ni: 2.0 mmol.

<sup>c</sup> 1: Aliquat 336.

<sup>d</sup> By gas chromatography; during the reactions 1–8 the distribution between the dichlorobenzenes remains unchanged.

<sup>e</sup> 100% after 50 min.

<sup>f</sup> 99% after 450 min (see Fig. 1).

<sup>g</sup> No reaction.

species and/or allowing different reaction environments. This effect seems to be crucial for the Ni-Raney catalyst.

In addition, DCBs (and also DBBs) are reduced at almost the same rate over Pd/C in the absence of 1. In its presence, a selective removal of the halogen is observed which varies according to the metal catalyst used. In fact, in the presence of Aliquat 336, the isomer reactivity of DCBs follows the order  $o \cong m > p$ ; that is, the *para* isomer is always the least reactive both with Pd/C and Ni-Raney (entries 1, 3, 5 and 7).

The same trend also holds in the hydrodebromination of DBBs over Ni-Raney (entries 13 and 14). Operating at 20°C the *p*-isomer reacts 4.5 fold slower than the *ortho*-one (entry 14).

When operating instead, with Pd/C, 1 induces a reverse reactivity on the DBB isomers by making the *ortho* derivative less reactive than the *para* one (entries 9 and 11). The effect is more pronounced at low temperatures (entry 11), where *o*-dibromobenzene reacts 2.0 fold slower than the *p*-dibromobenzene.

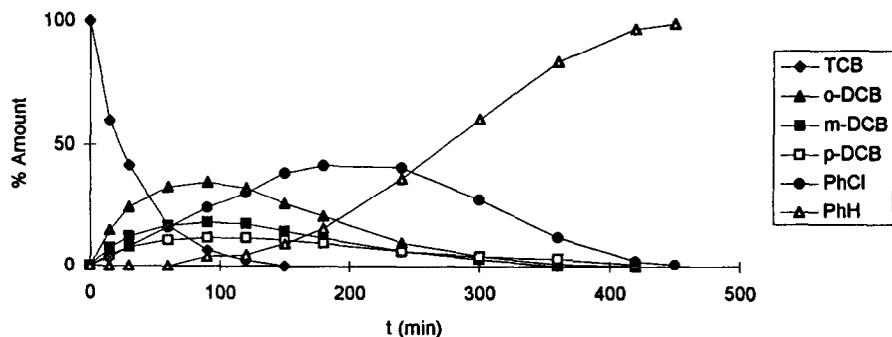


Fig. 1. Hydrodehalogenation of 1,2,4-trichlorobenzene in isooctane with Ni-Raney and Aliquat 336 (from Table 2, entry 5).

Table 3  
Catalytic hydrodehalogenation of 1,2,4-tribromobenzene under multiphase conditions <sup>a</sup>

Entry	Catalyst <sup>b</sup>	Solvent	PT agent <sup>c</sup>	T (°C)	t (min)	Conv. (%)	Yields (%)				
							Dibromobenzenes <sup>d</sup>			PhBr	PhH
							<i>ortho</i> -	<i>meta</i> -	<i>para</i> -		
1	Pd/C	Isooctane	1	50	50	97	9.0	1.0	–	2.0	85
2		Isooctane	no	50	40	94	30.0	3.0	1.0	18.0	42 <sup>e</sup>
3		<i>n</i> -Pentane	1	20	270	100	7.0	1.0	–	6.0	86
4		<i>n</i> -Pentane	no	20	50	99	7.0	1.0	–	16.0	75 <sup>f</sup>
5	Ni–Raney	Isooctane	1	50	10 (40)	100 (100)	1.0 (0.5)	24.0 (12.0)	61.0 (30.0)	14.0 (56.5)	– (1.0) <sup>g</sup>
6		Isooctane	no	50	180	39	1.5	11.0	24.0	2.0	–
7		Isooctane	2	50	15	100	2.0	21.0	61.0	16.0	– <sup>h</sup>
8		Isooctane	3	80	75	100	2.0	22.0	62.0	14.0	– <sup>i</sup>

<sup>a</sup> For reaction conditions see Experimental. TBB: 0.07 M (0.49 mmol).

<sup>b</sup> Pd: 0.015 mmol and Ni: 2.0 mmol.

<sup>c</sup> 1: Aliquat 336; 2: C<sub>16</sub>H<sub>33</sub>P<sup>+</sup>Bu<sub>3</sub>Br<sup>–</sup>; 3: C<sub>16</sub>H<sub>33</sub>N<sup>+</sup>(C<sub>18</sub>H<sub>37</sub>)<sub>3</sub>Br<sup>–</sup>.

<sup>d</sup> By gas chromatography; during the reactions 1–8 the distribution between the dibromobenzenes remains unchanged.

<sup>e</sup> 100% after 50 min.

<sup>f</sup> 100% after 60 min.

<sup>g</sup> 96% after 300 min.

<sup>h</sup> 98% after 150 min.

<sup>i</sup> 5% after 300 min.

### 3.2. Hydrodehalogenation of 1,2,4-trichlorobenzene and 1,2,4-tribromobenzene

In order to investigate the possible effects of the PT agent on the catalytic reduction of the polyhalogenated aromatics, several tests were per-

formed under multiphase conditions on 1,2,4-trichlorobenzene (TCB) and 1,2,4-tribromobenzene (TBB) using both Pd/C and Ni–Raney (Scheme 1).

In this case, due to the occurrence of consecutive dehalogenation reactions, in place of the

Table 4  
Hydrodehalogenation of 1-bromo-4-chlorobenzene under multiphase conditions <sup>a</sup>

Entry	Catalyst <sup>b</sup>	PT agent <sup>c</sup>	t (min)	Conv. (%)	Yields (%)	
					PhCl	Bz
1	Pd/C	1	35	100	69	31 <sup>d</sup>
2	Pd/C	no	50	97	88	9 <sup>e</sup>
3	Ni–Raney	1	90	100	80	20 <sup>f</sup>
4	Ni–Raney	no	–	–	–	– <sup>g</sup>

<sup>a</sup> All reactions were carried out in isooctane solution at 50°C. For details, see Experimental. 0.07 M (0.49 mmol) of substrate.

<sup>b</sup> Pd: 0.015 mmol and Ni: 2.0 mmol.

<sup>c</sup> 1: Aliquat 336.

<sup>d</sup> 100% after 50 min.

<sup>e</sup> 100% after 70 min.

<sup>f</sup> After 330 min: (5%) PhCl and (95%) benzene.

<sup>g</sup> No reduction after 360 min.

Table 5  
Hydrodehalogenation of 1-bromo-2,6-dichlorobenzene in multiphase systems <sup>a</sup>

Entry	Catalyst <sup>b</sup>	PT agent <sup>c</sup>	t (min)	Conv. (%)	Yields		
					<i>m</i> -DCB <sup>d</sup>	PhCl <sup>d</sup>	Bz <sup>d</sup>
1	Pd/C	1	80	100	23	8	69 <sup>e</sup>
2	Pd/C	no	35	99	25	16	58 <sup>f</sup>
3	Ni–Raney	1	10	100	100	0	0 <sup>g</sup>
4	Ni–Raney	no	180	10	10	0	0

<sup>a</sup> All reactions were carried out in isooctane solution at 50°C. For details, see Experimental. 0.07 M (0.49 mmol) of substrate.

<sup>b</sup> Pd: 0.015 mmol and Ni: 2.0 mmol.

<sup>c</sup> 1: Aliquat 336.

<sup>d</sup> DCB, PhCl and Bz: *m*-dichlorobenzene, chlorobenzene and benzene, respectively.

<sup>e</sup> 100% after 120 min.

<sup>f</sup> 100% after 45 min.

<sup>g</sup> After 300 min: *m*-DCB (80%) and PhCl (20%).



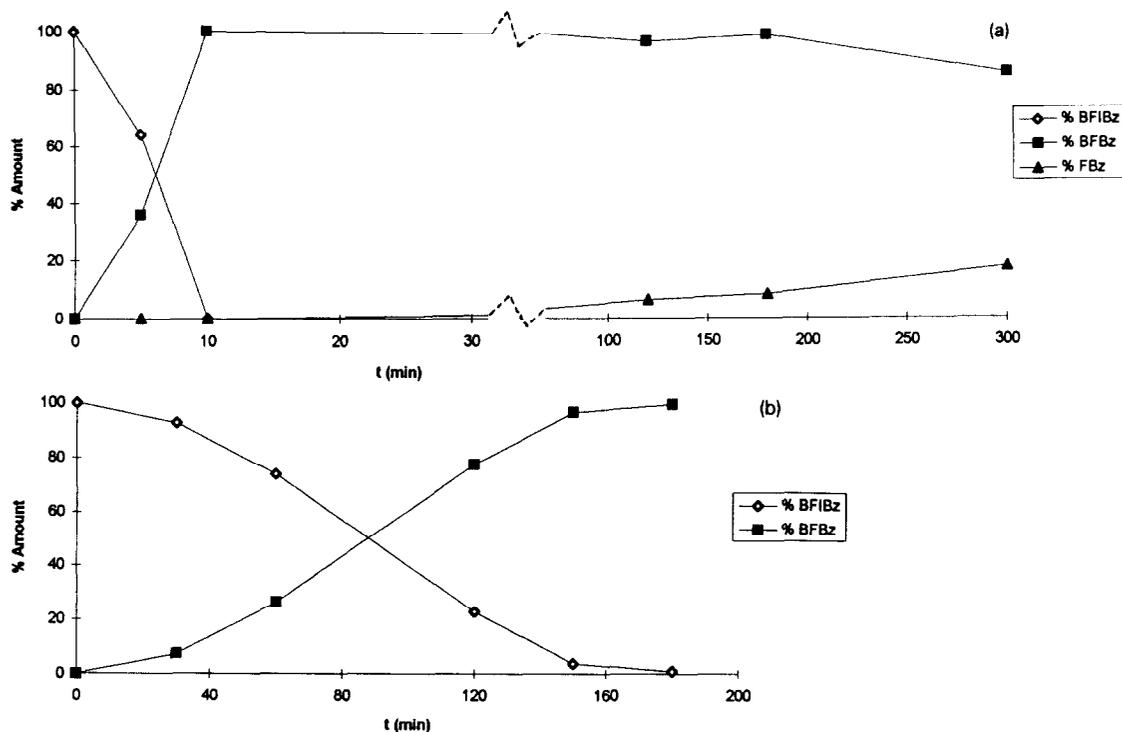


Fig. 2. (a) Hydrodehalogenation of 1-bromo-3-fluoro-4-iodobenzene (BFIBz) with Ni-Raney and Aliquat 336 (from Table 6, entry 3). (b) Hydrodehalogenation of 1-bromo-3-fluoro-4-iodobenzene (BIFBz) with Ni-Raney and without Aliquat 336 (from Table 6, entry 4).

the higher steric hindrance, the effect is more evident when BDCB is the substrate. In the case of the Ni catalyst, in particular, the very rapid and

Table 6  
Hydrodehalogenation of 1-bromo-3-fluoro-4-iodobenzene under multiphase conditions<sup>a</sup>

Entry	Catalyst <sup>b</sup>	PT agent <sup>c</sup>	t (min)	Conv. (%)	Yields (%)	
					BFB <sup>d</sup>	FB <sup>e</sup>
1	Pd/C	1	210	98	98	0 <sup>f</sup>
2	Pd/C	no	45	100	87	13 <sup>g</sup>
3	Ni-Raney	1	10	100	100	0 <sup>h</sup>
4	Ni-Raney	no	180	99	99	0 <sup>i</sup>

<sup>a</sup> All reactions were carried out in isooctane solution at 50°C. For details, see Experimental. 0.07 M (0.49 mmol) of substrate.

<sup>b</sup> Pd/C: 0.015 mmol and Ni: 2.0 mmol.

<sup>c</sup> 1: Aliquat 336.

<sup>d</sup> BFB: 1-bromo-3-fluorobenzene.

<sup>e</sup> FB: fluorobenzene.

<sup>f</sup> After 330 min only FB was present.

<sup>g</sup> 100% FB after 60 min and after 300 min 93% FB and 7% benzene.

<sup>h</sup> After 300 min 83% BFB and 17% FB.

<sup>i</sup> After 360 min 100% BFB.

selective bromine removal gives the pure *m*-DCB in the reaction mixture (entry 3, Table 5). Once again, the presence of onium salt 1 allows the Ni-Raney to be an effective and selective catalyst in the hydrodehalogenation reaction.

In addition, where selectivity is concerned, the effect of the halide anions originated from the reaction has also been considered. It is a well known concept in PT catalysis that quaternary onium salts allow a fast anion exchange between the two immiscible liquid phases. Moreover, if lipophilic anions are involved (e.g. I<sup>-</sup>), they are selectively transferred into the organic phase as counterions of the quaternary cations. Bearing this in mind, the hydrodehalogenation of 1-bromo-3-fluoro-4-iodobenzene (BFIBz) was investigated under our multiphase conditions. Table 6 reports the results.

In all cases, iodine is the first halogen to be removed. However, when Pd/C is the catalyst, an impressive decrease in catalytic activity results if

Aliquat is used (entry 1 and 2, Table 6). This behavior well parallels our previously reported observation [5]: the known poisoning effect of  $I^-$  on the Pd catalyst is markedly enhanced by the onium salt. In covering the metallic surface, the PT agent allows a higher  $I^-$  concentration on Pd thus inhibiting the further coordination with the reactants.

When Ni–Raney is used, the iodine removal is surprisingly rapid in the presence of **1** (entry 3, Table 6). However, immediately after hydroiodination is completed, a powerful inhibiting effect occurs. Fig. 2a–b clearly shows the course of the reaction. The reason of such different behaviour is unclear at the moment.

Although less evident with  $Br^-$  anions (less lipophilic than  $I^-$ ), the same effect might also be responsible for the slowing down of the TBB reduction (Table 3) and the selectivity in the *m*-DCB formation during the BDCB dehalogenation (Table 6), both situations occurring after an initial debromination.

#### 4. Conclusion

Under the investigated multiphase conditions, the presence of an onium salt markedly influenced the hydrodehalogenation of aromatics according to the compound to be reduced and the metal catalyst utilized.

The Ni–Raney catalyst is less active than the Pd/C one, since a high quantity of the former has to be used. Ni–Raney is also less active on mono- and dihalogenated benzenes; nevertheless, this may be particularly profitable to obtain selectively the less halogenated compounds when highly halogenated aromatics are reacted.

Different effects may result from the presence of the PT catalyst:

(1) Being adsorbed on the surface of the catalyst, the onium salt may mediate both the anion and the reagent/product exchanges with the two immiscible organic and aqueous phases. During the reaction, the originated halide anions may be quickly transferred into the aqueous phase thus

allowing catalyst regeneration (the metal surface being otherwise poisoned by the presence of the HX). In addition, the adsorbed onium salt provides a different reaction environment. This latter seems particularly suitable for the reactions using Ni–Raney, where reductions proceed (or proceed much better) only if the onium salt is present. Instead, the reaction rate is always depressed by the PT agent in the hydrodehalogenations carried out over Pd/C.

However, in all cases (both for Ni and Pd), the selectivity in the removal the halogen manifests itself only when the onium salt is present.

(2) The onium salt allows the influence of lipophilic anions (e.g.,  $I^-$ ,  $Br^-$ ) to be more efficient on the catalytic centers because it selectively transfers these anionic species from the aqueous phase to the metal catalyst. In our case, the effect of  $I^-$  is very clear: its presence together with the onium salt greatly inhibits the further debromination and dechlorination reactions, as shown in Fig. 2a–b.

It may be concluded that a proper combination of metal catalyst, onium salt and anionic species (produced or externally added into the reaction mixture) might give rise to the appropriate reaction environment to achieve high selectivity in halogen removal. In line with this, understanding of the reaction mechanisms will be crucial to elucidate the particular role of the PT agent.

In any case, the reported reactions represent a useful decontamination procedure for halogen removal from aromatics; in particular, the conditions described here may extend the application of Ni–Raney as an hydrodehalogenation catalyst [7].

In addition, the observed selectivity may render the method promising to give halogenated compounds not easily synthesized by direct electrophilic halogenation.

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