Facile Hydrodehalogenation with H₂ and Pd/C Catalyst under Multiphase Conditions. 2. Selectivity and Kinetics

Carlos Alberto Marques,* Maurizio Selva, and Pietro Tundo*

Dipartimento di Scienze Ambientali, Università di Venezia, Ca' Foscari, Calle Larga Santa Marta, 2137 - 30123 Venice, Italy

Received December 1, 1993

Hydrodehalogenation of polyhalogenated aromatics with Pd/C catalyst carried out in the presence of a quaternary onium salt follows zero-order kinetics in the substrate and first-order kinetics in the Pd/C catalyst; the related rate constants were determined for o-, m- and p-bromotoluenes, o-, m- and p-chloroalkylbenzenes (methyl, ethyl, and propyl derivatives), and other aryl halides. Reaction rates, depending on the aromatic to be reduced, may be strongly enhanced by the presence of a quaternary onium salt. The isomer chloroethylbenzenes were reduced 50 times faster when operating in the presence of Aliquat 336 (1). Also the hindered 2-chloro-m-xylene easily yielded m-xylene. The cocatalyst onium salts operate by being adsorbed on the Pd/C surface, as shown when kinetic constants are reported by varying the onium salt amount; classical Langmuir adsorption isotherms are observed. The presence of the onium salt may also influence selectivity in the reduction of isomeric aryl halides: when 1 is present, p-dichlorobenzene reacts in diethyl ether at 20 °C, 5-fold slower than the ortho isomer; whereas the reduction rates of the two compounds are almost the same in its absence.

Introduction

We have previously reported that facile hydrodehalogenation of polyhalogenated aromatics occurs when the reaction is carried out under multiphase conditions and in the presence of a quaternary onium salt: operating in a 50% KOH/isoctane two-phase system along with a Pd on carbon (Pd/C) catalyst and hydrogen at atmospheric pressure, 1,2,4,5-tetrachlorobenzene was reduced to benzene in 30 min at 50 °C (1:130 Pd/C).1

Hydrodechlorination reactions compared to other detoxification methods2a-3a-s are gaining in importance because they allow the polyhalogenated aromatics to be reduced to the parent hydrocarbons without the production of waste. Moreover, they may selectively remove halogen from the aromatic ring, thus providing new methods for organic synthesis.

In addition to Pd-promoted reactions,2 such hydrodehalogenations have also been catalyzed by many complexes of Rh and Pt,4 but, even when operating with the more highly active catalysts [(Cy2P)Rh(H)Cl2; Cy = cyclohexyl], hindered compounds such as tetrachloro-m-xylene and 2-chlorotoluene were scarcely reactive.5

1 Supported by National Council Research of Brazil (CNPq).
7 (x) Grushin, V. V.; Alper, H. Organometallics 1981, 10, 1620.

Scheme 1

<table>
<thead>
<tr>
<th>(C₆H₅)(CH₂)₃N⁺CH₂Cl⁻</th>
<th>CH₃(CH₂O)₃CH₂O,H⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Aliquat 336</em></td>
<td>poly(ethylene glycol) monomethyl ether; n ~ 15</td>
</tr>
</tbody>
</table>

We report here a preliminary kinetic investigation of hydrodehalogenation reactions carried out under multiphase conditions. Particularly, these reaction conditions have also proven to be successful for the dehalogenation of 2-chlorotoluene and other unreactive compounds (Tables 1, 3 and 6). Polychlorinated biphenyls (PCBs) are also quickly reduced to biphenyl. The effect of the added quaternary onium salt in changing both the reaction rate and the selectivity in the removal of different halogens is considered.

The dehalogenation of several monochlor derivatives is at first examined and the related kinetic parameters are reported. Then, competitive reactions of some monochlorinated isomeric alkylbenzenes are discussed with respect to the presence of Aliquat 336 (tricaprolyltrimethylammonium chloride (1) in Scheme 1).

Selectivity in the removal of different halogens bonded to the same aromatic ring (i.e., o-, m- and p-dichlorobenzene, 2-chloro-1-fluoro-4-iodobenzene, etc.) is reported as well as the poisoning effect on the reaction rate of a few inorganic salts.

Results and Discussion

All reactions were carried out in a 25-mL three-necked round-bottom flask equipped with a condenser and a system for the bubbling of hydrogen.

If not otherwise indicated, they were carried out on 7.0 mL of a 0.07 M isooctane solution of the substrate (0.49 mmol) to be reduced (2-chloro-o-xylene, 2-chloro-m-xylene, 2-chloro-p-xylene, p-bromophenyl, 1-chloronaphthalene, and chlorobenzene).

Competitive reactions (see later) were performed on 7.0 mL of a solution, 0.07 M for each of the isomeric...
Multiphase Hydrodehalogenation with \( \text{H}_2 \) and Pd/C Catalyst compounds (1.47 mmol in total), \( n \)-decane being the internal standard.

In all cases 4.0 mL of 50% KOH aqueous phase solution and 0.032 g of 5% Pd/C (0.015 mmol of Pd) were used (except Figure 1b).

The amount of onium salts varied according to the experiments; but usually it was 0.20 mmol.

Hydrogen was bubbled at atmospheric pressure through the organic phase at a rate of about 1 mL/min; as previously reported, under such conditions, the reaction rates were not dependent on this \( \text{H}_2 \) inlet.

The reaction flask was thermostated at 50 \( \pm \) 0.1 °C (if not otherwise indicated), and the mixture was magnetically stirred at 1000 rpm with a bar of 2.5 cm in length and 0.6 cm in diameter.

The stirring of the solution and the form of the reaction vessel play an important role in the distribution of Pd/C catalyst in the whole reaction mixture and therefore in the reaction rates. Furthermore, under our conditions, when a phase transfer (PT) agent is used, a particular physical disposition of the Pd/C catalyst is observed: the metallic catalyst is aggregated in the organic phase alone. When the amount of PT agent is increased, it places itself in the interface having become insoluble in both the organic and aqueous phases: at this point, the Pd/C is visibly embodied by the onium salt.

On the contrary, when no onium salts are used, the Pd/C catalyst appears uniformly disposed, under stirring, in the whole reaction mixture. However, both in the presence and the absence of onium salts, we checked that reduction rates, under our conditions, were not diffusionally controlled (see separate material).

The reaction course was followed by gas chromatography. Conversions are referred to the internal standard (see Experimental Section for calibration).

2-Chloro-\( m \)-xylene (eq 1) was chosen as a model compound for kinetics determinations: its low reactivity (see also ref 5) allowed the reaction to be followed more accurately.

\[
\begin{align*}
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{Cl} \\
\text{CH}_3 \quad \text{CH}_3
\end{array} & \xrightarrow{\text{H}_2, \text{Pd/C, KOH, aqueous}} \quad
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_3 \\
\text{CH}_3
\end{array}
\end{align*}
\]

Equation 1

Figure 1a reports the advancement of the reaction of 2-chloro-\( m \)-xylene to \( m \)-xylene. Zero-order kinetics with respect to the substrate is evident. Figure 1b shows the linear relationship between the zero-order constants and the amount of catalyst used in the reaction: this dependence suggests that the rate-determining step is chemisorption of the substrate on the Pd/C catalyst. The reaction rate, as already reported, is strongly dependent on the steric factors: the actual conditions also allow 2-chloro-\( m \)-xylene to be quickly reduced.

Table 1 reports the hydrodechlorination of several monochloro aromatics. All the substrates follow correct pseudo zero-order kinetics \( (r > 0.99) \). Reaction rates clearly depend on the steric hindrance: methyl groups always decrease the reaction rate, but more relevantly when in the ortho position; notably for comparison, after 18 h at 60 °C, only 7% of \( o \)-chlorotoluene was reduced to toluene when using 1 mol % of \( (\text{Cy}_3\text{P})_2\text{Rh(H)Cl}_2 \). The reaction proceeds, as already known, via adsorption of

![Figure 1.](image)
Table 1. Pseudo-Zero-Order Rate Constants in the Hydrodehalogenation of Several Chlorinated Aromatics under Multiphase Conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>reagent</th>
<th>$k \times 10^4$ (M s$^{-1}$)</th>
<th>product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>chlorobenzene$^b$</td>
<td>101</td>
<td>benzene</td>
</tr>
<tr>
<td>2</td>
<td>p-chlorotoluene</td>
<td>63</td>
<td>toluene</td>
</tr>
<tr>
<td>3</td>
<td>1-chloronaphthalene$^b$</td>
<td>15</td>
<td>naphthalene</td>
</tr>
<tr>
<td>4</td>
<td>4-chloro-o-xylene</td>
<td>54</td>
<td>o-xylene</td>
</tr>
<tr>
<td>5</td>
<td>2-chloro-m-xylene$^c$</td>
<td>1.2</td>
<td>m-xylene</td>
</tr>
<tr>
<td>6</td>
<td>2-chloro-p-xylene$^c$</td>
<td>16</td>
<td>p-xylene</td>
</tr>
</tbody>
</table>

$^a$ All reactions were carried out using an isocanate solution of the substrate (7.0 M; 0.07 M), KOH$\text{aq}$ (4.0 M; 50%); 5% Pd/C (0.085 g; 0.015 mmol of Pd), and Aliquat 336 (0.085 g; 0.20 mmol).

$^b$ From ref 1. $^c$ From Figure 1.

the aryl halide on the carbon, where the Ar–X bond is reduced by H$_2$.

Moreover, no coupling reaction takes place: in fact, biphenyl wasn’t detected in the dechlorination of chlorobenzene (entry 1, Table 1: biphenyl less than 0.1%). Under such conditions, we also previously reported$^d$ that no aromatic nucleophilic substitution occurs: no H/D exchange was observed.

Entry 2 of Table 1 has to be compared with the result of Table 3, entry 4, where p-chlorotoluene was reacted together with ortho and meta isomers. It is shown that the reaction rate of Table 1 (63 to $10^{-4}$ M s$^{-1}$) corresponds well with 22 to $10^{-4}$ M s$^{-1}$, if one considers that in the Table 3 only one-third of the Pd/C catalyst was used in comparison.

In order to study the selectivity in the dehalogenation, competitive reactions between many reagents were considered, because more reliable results can be obtained. However, when many polychlorinated compounds are contemporaneously reacted, the calculation of the kinetic constants may be problematic due to possible consecutive reactions which may interfere each other. This difficulty has been overcome by examining the dechlorination of three dichlorobenzene isomers: in fact, a unique intermediate (chlorobenzene) and a sole final product (benzene) are produced.

According to this, Table 2 reports the competitive hydrodehalogenation of o-, m-, and p-dichlorobenzenes in different organic solvents and temperatures, both in the presence and the absence of Aliquat 336. Correct pseudo zero-order constants can be determined in the reaction of the three isomers; for simplicity, only the kinetic constant for the ortho isomer is reported ($k_{\text{ortho}}$) and the ratios $k_{\text{meta}}/k_{\text{ortho}}$ and $k_{\text{para}}/k_{\text{ortho}}$ are shown; that is, in entry 1 of Table 2, $k_{\text{ortho}} = k_{\text{ortho}} \times 1.04 = 66$ M/s and $k_{\text{para}} = k_{\text{ortho}} \times 0.71 = 45$ M/s. The time required for the dichlorobenzene mixture to be reduced to benzene is also reported.

In the presence of the onium salt, the reaction rate may either decrease or increase. Particularly, a negative effect is pronounced in apolar solvents at higher reaction temperatures (50 °C; entries 1, 2 and 8, 9). Instead, when comparing reaction rates at low temperatures (20 °C), an increase is observed using diethyl ether (entries 3–7 and 10).

On the other hand, the presence of the PT agent seems to induce a selective removal of the chlorine atoms among the isomeric compounds. In fact, in the absence of 1, the dichlorobenzenes react at almost the same rate (entries 2, 5, 7, and 9). Instead, when Aliquat 336 is present, o-dichlorobenzene is always more reactive than the para isomer (entries 1, 3, 4, 6, 8, and 10). As usual, selectivity increases by lowering the temperature (compare entries 1 with 3 and 8 with 10). However, operating at 20 °C, even though differences are not so overwhelming, more significant selectivity is observed in diethyl ether where the reaction is faster. Particularly, the o-dichlorobenzene reacts 5.3 times faster than the para isomer (entry 4).

Table 3 reports the competitive hydrodehalogenation of o-, m-, and p-chloroalkylbenzenes (eq 2) in different solvents and temperatures, operating either with or without the Aliquat 336 or polyethylene glycol monomethyl ether (PEG 550; 3 in Scheme 1).

When operating in isooctane at 50 °C, the presence of 1 markedly enhances the reaction rate of the ethyl and propyl isomers (from 18 to 48 times faster; entries 2, 3, and 5, 6) while no increase is shown for chloromethylbenzenes (entries 1 and 4).

A similar behavior is also observed in diethyl ether at 20 °C, but differences in rates are rather smaller: the ortho isomers react only 2 times faster when Aliquat 336 is present (entries 8–13). In this case, the trend also holds for methyl derivatives (entries 8 and 11). Noticeably, at low temperature (20 °C), in diethyl ether, reaction rates seem to show a dependence on the length of the alkyl chain in the aromatic: an increase in the length results in a decrease in the rates (entries 8–10 and 11–13). At 20 °C, in n-pentane, 1 slightly improves the reduction rate of chlorotoluenes (entries 16 and 17).

In the presence of 3, hydrodehalogenation is always slowed down (compare entries 8 and 14, 10 and 15).

As selectivity is concerned, the presence of the onium salt 1 has no great effect. However, looking at the general trend, 1 seems to induce a reverse reactivity by making the para isomers (usually the most reactive because less hindered) less reactive than the ortho ones (compare entries 1–3 and 4–6; 8–10 and 11–13).

Table 4 reports the reaction with three isomeric bromotoluenes. The Q$^+$X$^-$ agent was in this case either compound 1 or 2. Even though effects on selectivity between the bromotoluenes are relatively low, again (as occurs for chlorobenzenes) 1 and 2 tend to produce a reverse reactivity that is, para isomers become less reactive than ortho ones. Reaction rates, if compared with the corresponding chlorotoluenes (Table 4, entries 1, 4, 8, and 11), are lower. This might be attributable to an effect of Br$^{-}$ (see Table 5).

Figure 2 reports the rate constants of the competitive hydrodehalogenation of the o-, m-, and p-chloroalkylbenzenes mixture by varying the concentration of Aliquat 336 in isooctane. An evident rate enhancement is observed by increasing the PT agent amount (compare also Table 3, entries 2 and 5). The rate constants appear quite well arranged according to adsorption isotherms (Langmuir isotherms); they increase almost linearly with the onium salt concentration until constant values are reached (at about 13 molecules of 1 per Pd atom) when, presumably, the solid carbon surface is saturated by 1.

Figure 2 also shows that besides the rate enhancement, the increase in the amount of PT agent to some extent, alters selectivity as well. In fact, three different plateaux,

Multiphase Hydrodehalogenation with H₂ and Pd/C Catalyst

**Table 2. Pseudo-Zero-Order Rate Constants for Competitive Hydrodehalogenations of o-, m-, and p-Dichlorobenzenes in Different Multiphase Systems**

| entry | solvent | PT agent | T (°C) | kortho × 10⁴ (M s⁻¹) | (kortho:kmeta:kpara) | t (min) | % benzene
|-------|---------|----------|--------|-----------------------|---------------------|---------|----------
| 1     | isooctane | 1        | 50     | 63                    | 1.00:0.94:0.71     | 60      | 100      |
| 2     | isooctane | no       | 50     | 97                    | 1.00:0.95:0.99     | 50      | 99       |
| 3     | isooctane | 1        | 20     | 3.0                   | 1.00:0.98:0.48     | 180     | 97       |
| 4     | diethyl ether | 1        | 20     | 10                    | 1.00:0.89:0.21     | 90      | 100      |
| 5     | diethyl ether | no       | 20     | 9.4                   | 1.00:1.14:1.12     | 90      | 98       |
| 6     | n-pentane | 1        | 20     | 6.7                   | 1.00:1.05:0.44     | 150     | 97       |
| 7     | n-pentane | no       | 20     | 7.0                   | 1.00:0.99:0.99     | 130     | 92       |
| 8     | n-hexane | 1        | 50     | 11                    | 1.00:1.18:0.84     | 60      | 100      |
| 9     | n-hexane | no       | 50     | 22                    | 1.00:0.94:1.01     | 35      | 98       |
| 10    | n-hexane | 1        | 20     | 4.2                   | 1.00:1.04:0.58     | 150     | 96       |

* a For reaction conditions, see Experimental Section in General Procedure for Competitive Reactions. b Zero-order reaction rates for o-dichlorobenzene. c Normalized ratio between corresponding rate constants for ortho, meta, and para isomers, respectively (kortho is set equal to unity).

**Table 3. Competitive Hydrodehalogenation of o-, m-, and p-Chloroalkylbenzenes in Different Multiphase Systems (eq 2)**

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>alkyl group</th>
<th>T (°C)</th>
<th>kortho × 10⁴ (M s⁻¹)</th>
<th>(kortho:kmeta:kpara)</th>
<th>product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no</td>
<td>CH₃</td>
<td>50</td>
<td>23</td>
<td>1.00:1.38:1.27</td>
<td>toluene</td>
</tr>
<tr>
<td>2</td>
<td>no</td>
<td>CH₃CH₃</td>
<td>50</td>
<td>0.6</td>
<td>1.00:1.13:1.19</td>
<td>ethylbenzene</td>
</tr>
<tr>
<td>3</td>
<td>no</td>
<td>CH₃CH₂CH₂CH₃</td>
<td>50</td>
<td>1.2</td>
<td>1.00:1.16:1.20</td>
<td>n-propylbenzene</td>
</tr>
<tr>
<td>4</td>
<td>isooctane</td>
<td>CH₃</td>
<td>50</td>
<td>22</td>
<td>1.00:0.98:0.91</td>
<td>toluene</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>CH₃CH₂CH₃</td>
<td>50</td>
<td>29</td>
<td>1.00:0.97:0.73</td>
<td>ethylbenzene</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>CH₃CH₂CH₂CH₃</td>
<td>50</td>
<td>22</td>
<td>1.00:0.90:0.61</td>
<td>n-propylbenzene</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>CH₃</td>
<td>20</td>
<td>4.6</td>
<td>1.00:1.11:1.33</td>
<td>toluene</td>
</tr>
<tr>
<td>8</td>
<td>no</td>
<td>CH₃</td>
<td>20</td>
<td>6.6</td>
<td>1.00:1.28:1.23</td>
<td>toluene</td>
</tr>
<tr>
<td>9</td>
<td>no</td>
<td>CH₃CH₂CH₃</td>
<td>20</td>
<td>5.8</td>
<td>1.00:1.03:0.99</td>
<td>ethylbenzene</td>
</tr>
<tr>
<td>10</td>
<td>no</td>
<td>CH₃CH₂CH₂CH₃</td>
<td>20</td>
<td>3.7</td>
<td>1.00:1.02:0.99</td>
<td>n-propylbenzene</td>
</tr>
<tr>
<td>11</td>
<td>diethyl ether</td>
<td>CH₃</td>
<td>20</td>
<td>14</td>
<td>1.00:1.09:0.97</td>
<td>toluene</td>
</tr>
<tr>
<td>12</td>
<td>no</td>
<td>CH₃CH₂CH₃</td>
<td>20</td>
<td>12</td>
<td>1.00:1.03:0.92</td>
<td>ethylbenzene</td>
</tr>
<tr>
<td>13</td>
<td>no</td>
<td>CH₃CH₂CH₂CH₃</td>
<td>20</td>
<td>7.5</td>
<td>1.00:1.05:0.96</td>
<td>n-propylbenzene</td>
</tr>
<tr>
<td>14</td>
<td>3</td>
<td>CH₃</td>
<td>20</td>
<td>0.5</td>
<td>1.00:1.41:0.69</td>
<td>toluene</td>
</tr>
<tr>
<td>15</td>
<td>3</td>
<td>CH₃CH₂CH₃</td>
<td>20</td>
<td>2.9</td>
<td>1.00:1.01:1.02</td>
<td>n-propylbenzene</td>
</tr>
<tr>
<td>16</td>
<td>n-pentane</td>
<td>CH₃</td>
<td>20</td>
<td>8.2</td>
<td>1.00:1.08:1.05</td>
<td>toluene</td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>CH₃</td>
<td>20</td>
<td>11</td>
<td>1.00:1.04:0.85</td>
<td>toluene</td>
</tr>
</tbody>
</table>

* a For reaction conditions, see Experimental Section in General Procedure for Competitive Reactions. b Zero-order rate constants for the ortho isomers. c Normalized ratio between corresponding rate constants for ortho, meta, and para isomers, respectively (kortho is set equal to unity).

**Table 4. Pseudo-Zero-Order Rate Constants for Competitive Hydrodehalogenation of o-, m-, and p-Bromotoluene in Different Multiphase Systems**

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>PT agent</th>
<th>T (°C)</th>
<th>kortho × 10⁴ (M s⁻¹)</th>
<th>(kortho:kmeta:kpara)</th>
<th>t (min)</th>
<th>% toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>isooctane</td>
<td>1</td>
<td>50</td>
<td>10</td>
<td>1.00:1.01:0.97</td>
<td>80</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>isooctane</td>
<td>no</td>
<td>50</td>
<td>50</td>
<td>1.00:1.06:1.04</td>
<td>25</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>25</td>
<td>25</td>
<td>100:0.94:0.85</td>
<td>50</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>6.8</td>
<td>18</td>
<td>1.00:0.96:0.88</td>
<td>110</td>
<td>91</td>
<td></td>
</tr>
</tbody>
</table>

* a For reaction conditions, see Experimental Section in General Procedure for Competitive Reactions. b Zero-order rates for o-bromotoluene. c Normalized ratio between corresponding rate constants for ortho, meta, and para isomers, respectively (kortho is set equal to unity).

**Table 5. Competitive Hydrodehalogenation of o-, m-, and p-Chloroethylenbenzene in the Presence of an Inorganic Salt**

<table>
<thead>
<tr>
<th>entry</th>
<th>salt added</th>
<th>T (°C)</th>
<th>kortho × 10⁴ (M s⁻¹)</th>
<th>(kortho:kmeta:kpara)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no salt added</td>
<td>50</td>
<td>29</td>
<td>1.00:0.97:0.73</td>
</tr>
<tr>
<td>2</td>
<td>KF</td>
<td>1</td>
<td>1.6</td>
<td>1.00:1.04:0.98</td>
</tr>
<tr>
<td>3</td>
<td>KBF₄</td>
<td>11</td>
<td>1.00:1.06:0.99</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>HBF₄</td>
<td>14</td>
<td>1.00:0.97:0.92</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>NaBO₂H₂O⁴</td>
<td>18</td>
<td>1.00:0.95:0.88</td>
<td></td>
</tr>
</tbody>
</table>

* a All reactions were carried out under multiphase conditions, in isooctane solution, using 5% Pd/C and Aliquat 336 (for details, see Experimental Section). b Zero-order rate constants for o-chloroethylenbenzene. c Normalized ratio between corresponding rate constants for ortho, meta, and para isomers, respectively (kortho is set equal to unity). d From Table 4, entry 5. e KI, 0.1 g / KBr, 0.1 g. f KBF₄, 0.03 g. g NaBO₂H₂O₄, 0.1 g.

That is three different rate maxima, are reached at 29, 28, and 21 × 10⁻⁴ M s⁻¹ for o-, m-, and p-chloroethylenbenzenes, respectively. Instead, the three isomers react at almost the same rate in the absence of 1 (0.6 M s⁻¹).

Therefore, the adsorption of 1 on Pd/C seems to play a decisive role in determining the observed pattern for the rate constants. In coating the insoluble catalyst, the ionium salt might create a more favorable reaction environment either by improving the adsorption of the aryl chlorides (or hydrogen) or by discriminating on the species to be easily adsorbed among isomeric chlorinates; in this way, reaction rate and selectivity may contemporarily increase.

A similar adsorption behavior is reported in Figure 3 where the rate constants for the hydrodebronomisation of 4-bromobiphenyl (eq 3) are plotted versus the amount of the used PT agent (2 in Scheme 1).

4-bromobiphenyl

A Langmuir isotherm can be drawn indicating that in the explored range of concentration, the reaction rate
Figure 2. The rate constants for the competitive hydrodehalogenation of o-, m-, and p-chloroethylbenzenes mixture are reported by varying the amount of the aliquat 336. All rate constants were determined by carrying out the reaction under multiphase conditions at 50 °C, in isooctane solution and using 5% Pd/C (for details see Experimental Section and Table 3, entry 5). The $k_i$ molar ratio was ranged from 0 to 26.6 (0.170 g of 1).

Increases by increasing the onium salt amount, until a plateau is reached. However, when no PT agent is used, the reaction takes place more rapidly (note the point at abscissa zero and the dashed line). At the moment, this behavior is quite unclear. The concentration of the onium salt seems still important in controlling the adsorption of the reagents but, in this case, its positive effect (shown by the positive slope in the Langmuir isotherm) is not sufficient to improve the reaction rate over the value observed for Pd/C alone. This might be due to the different cationic structure $[n$-$C_{18}H_{33}P^+{(Bu)}_3]$ of 2 or the anion involved (Br-) in the reaction (see later, Table 5).

In order to preliminarily investigate the possible interaction of the PT agent with the metallic catalyst and its role in our multiphase system, the hydrodehalogenation of 2-chloro-1-fluoro-4-iodobenzene was studied. This reaction can originate three different anionic species (Cl-, F-, I-) and therefore it could be particularly suitable to analyze the behavior of the quaternary onium salts. In fact, it is well known in PT catalysis, that surfactants produce a fast anion exchange between two immiscible liquid phases.

Figure 3. Rate constants for the hydrodeboronation of 4-bromobiphenyl are reported by varying the amount of hexadecyltributylphosphonium bromide (2). All reaction constants were determined by carrying out the reaction under multiphase conditions at 50 °C, in isooctane solution and using 5%-Pd/C (for details see Experimental Section). The $k_i$ molar ratio was ranged from 0 to 34.6 (0.27 g of 2). The dashed line is used to remark the rate constant value in the absence of 2.

Figure 4 shows the behavior of the hydrodehalogenation reaction on 2-chloro-1-fluoro-4-iodobenzene (eq 4) in the absence of the onium salt. Iodine is the first halogen to be removed.

$$\text{2-chloro-1-fluoro-4-iodobenzene}$$

When iodine has completely come out (after 20 min), the reaction mixture is constituted by 87% of 2-chlorofluorobenzene and 13% by fluorobenzene. Then chlorine reacts; when 2-chlorofluorobenzene has disappeared (after 75 min), the reaction mixture is composed of 78% fluorobenzene and 22% by benzene. Finally, after 4 h of reaction, only benzene is present.
Multiphase Hydrodehalogenation with H₂ and Pd/C Catalyst

In coating the Pd/C catalyst, the quarternary onium salt modifies the reaction environment: adsorption phenomena of the reactants over the catalyst surface seems actually mediated by its presence.

However, the results obtained up to now make it difficult to foresee the behavior of different halogenated compounds under our reaction conditions. In particular, the dependence of the reaction rate on the PT agent structure and the solvent, in relation to the structure of the reagent species, is very hard to comprehend. Nevertheless, when operating in the presence of a PT agent, some general considerations stand out: (i) in some cases, the proper choice of the solvent and the reaction temperature may result in a marked enhancement of the reaction rate; (ii) lipophilic anions may be introduced in the metal surface by promoting a fast transport of the produced halide anion in the aqueous phase. Thus, during the reaction, a higher concentration of compounds to be reduced may be present on the metallic surface: an increased reaction rate results.

However, when poisoning lipophilic specie may originate from the reaction products (for example, I⁻), the PT agent exalts the induced inhibiting effect by probably blocking these specie on the metallic surface. An increased reaction rate results.

Table 5 gives better evidence for such an effect: competitive hydrodehalogenation of o-, m-, and p-chloroethylbenzenes is reported, operating with Aliquat 336 and in the additional presence of an inorganic salt. It is shown that all the added salts lowered the reaction rate and at the same time decreased the selectivity, thus approaching the results obtained operating in the absence of the PT agent (see Table 5, entry 2); in particular, the more lipophilic the anion, the lower the reaction rate is. This suggests that in general the anion is preferably retained by the insoluble catalyst in place of the halogenated compounds.

Our hydrodehalogenation method has been successfully applied to other hindered compounds: mixtures of PCBs (Aroclor 1254) are quickly reduced to biphenyl. Table 6 reports the hydrodehalogenation of PCBs (eq 5). Under such multiphase conditions a fast reaction takes place, if operating in the presence of Aliquat 336.

In fact, starting with a 35 000-ppm solution of PCBs (Aroclor 1254) in isooctane, after 3.0 h of reaction at 50°C, the PCBs were reduced to biphenyl. When the PT agent is used, the acceleration of the hydrodechlorination reaction is evident (compare entries 1 and 2). The source of the hydrogen may also be a hypophosphite salt (entry 3), which is decomposed by the same Pd/C catalyst to hydrogen, as was previously reported on such conditions.10

Conclusions

In the presence of a PT agent, hydrodehalogenation reactions carried out under a multiphasic system show different reaction outcomes, as reaction rate and selectivity are concerned.

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Conclusions
Experimental Section

All reagents and solvents were ACS grade and were used without further purification. o-, m-, and p-chloroanisole and o-, m-, and p-chloroanisole were synthesized (see later). Melting points were determined on Buchi 535 melting point apparatus and are uncorrected. 5% Pd/C was from Fluka, Art. No. 75992; its surface area was 700–800 m²/g. GC analyses were performed on a Varian GC 3400 using a fused silica capillary column (30 m × 0.25 mm) with SPB-5 as liquid phase (film thickness 0.25 mm). GC/MS analyses were performed on a HP 5971 mass detector coupled to a HP 5890 gas chromatograph fitted with a 30 m × 0.25 mm DBS capillary column.

Preparation of o-, m-, and p-Chloro-n-propylbenzene and o-, m-, and p-Chloroethylbenzene. These compounds were prepared according to the literature.

\textbf{m-Nitro-n-propylbenzene (4).} Propiophenone (60.5 g, 0.45 mol) was nitrated with HNO₃ (300 mL, d = 1.5) in acetic acid (8.0 mL) from −10 to 0 °C and after recrystallization from ethanol, 4 was obtained in 70% yield (94% pure by GC; mp = 101–102 °C).\(^1\)

\textbf{m-Aminopropiophenone (5).} m-Nitropropiophenone (4) (21.5 g, 0.45 mol) was reduced in glacial acetic acid (60 mL) with SnCl₂ (100 g) in hydrochloric acid (240 mL, 7.5 N).\(^1\) The amine (96% pure by GC, 96% yield) is a solid (mp = 73–75 °C); the structure was verified by mass spectroscopy (70 eV) m/z (relative intensity): 149 (M⁺, 56), 120 (100), 92 (69), 65 (22).

\textbf{m-Chloropropiophenone (6).} 5 (10 g, 0.067 mol) was diazotized using standard conditions.\(^1\) The obtained aqueous solution was poured rapidly, at 0 °C, into a well-stirred cuprous chloride solution (8.23 g in 25 mL HCl). The product\(^6\) was washed with water and extracted with diethyl ether; after evaporation of the solvent, a solid was obtained (7 g, 70% yield; mp = 46–48 °C); mass spectrum (70 eV) m/z (relative intensity): 170 (6), 168 (M⁺, 18), 141 (31), 139 (100), 113 (13), 111 (39), 75 (18).

\textbf{m-Chloromethylbenzene (7).} m-Chloromethylphenol (6) was reacted according to the Wolf–Kishner procedure.\(^1\) 6 (3.5 g, 0.021 mol) in triethylene glycol (27 mL) was heated at 91–95 °C with KOH (3.5 g) and hydraxine hydrate (2.7 mL; 85%). The product was removed by means of take-off adapter. The product 7 was washed with H₂O and diethyl ether, dried over Na₂SO₄, and distilled (86% pure by GC, 62% yield; bp₀ = 80 °C); mass spectrum (70 eV) m/z (relative intensity): 156 (11), 154 (M⁺, 35), 127 (94), 125 (100), 91 (24), 85 (25).

\textbf{a- and p-Chloropropiophenones, as well as o-, m-, and p-chloroanisoles} were prepared from the corresponding aminopropiophenones (Aldrich Art. No. 23,733–7; 23,734–5; E1,180–3; E1,200–1; and 17,549–8, respectively) by classical Sandmeyer procedures.\(^1\) They had the following bp₀: 90–92 °C (93% pure by GC, 75% yield), 85–88 °C (98% pure by GC, 82% yield), 79–81 °C (94% pure by GC, 78% yield), 79–81 °C (97% pure by GC, 70% yield), and 84–86 °C (99% pure by GC, 89% yield), respectively.

**GC Analyses. Calibration.** Ten 0.07 M solutions of p-chlorotoluene plus toluene in isooctane were prepared, having different molar compositions (from 95/5 to 5/95 ratio of two substrates), and analyzed by gas chromatography. The experimentally obtained ArCl/ArH ratio were plotted against the theoretical value; a linear plot, passing through the origin, was obtained (r = 0.997).

**Preparation of Gas Chromatographic Samples.** (i) Aryl Halides. A few drops (about 0.05 mL) of the reaction mixture were diluted in diethyl ether (≈0.8 mL). To this solution, silica gel (≈0.1 g), and Na₂SO₄ (≈0.15 g) were added. Finally, the liquid phase was filtered by a Pasteur pipette fitted with a small wool cotton pellet at the end. This solution was analyzed by GC (0.2 μL).

(ii) Polychlorinated Biphenyls. A few drops (about 0.1 mL) of the reaction mixture were diluted in isooctane (≈2.0 mL). To this solution, were added silica gel (≈0.05 g) and Na₂SO₄ (≈0.5 g). Finally, the liquid phase was filtered by a Pasteur pipette fitted with a small wool cotton pellet at the end. This solution was analyzed by GC (0.2 μL).

**General Procedure for Hydrodechlorination of 2-Chloro-m-xylene, 4-Chloro-m-xylene, 4-Chloro-o-xylene, Chlorobenzene, 1-Chloronaphthalene, and 4-bromobiphenyl (Tables 1 and 5 and Figures 1a, 1b, and 3).** In a 25-mL three-necked round-bottomed flask thermostated at 50 ± 0.1 °C and connected with a system for the addition of hydrogen, a mixture of KOH aqueous solution (4.0 mL, 50%), 5% Pd/C (0.032 g; 0.015 mmol of Pd), and PT agent (0.20 mmol); in the cases of Figures 1a and 1b, and in all the entries of Table 1 was magnetically stirred at 1000 rpm. In the other cases (Figures 2 and 3), the amount of nium salts varied according to experiments. A volume of 7.0 mL of the specific organic solution, containing n-decane as internal standard, was added. Hydrogen was bubbled at atmospheric pressure in the organic phase at about 1 mL/min.

**General Procedure for the Competitive Reactions (Tables 2–5 and Figure 2).** In a 25-mL three-necked round-bottomed flask thermostated at 50 ± 0.1 °C and connected with a system for the addition of hydrogen, a mixture of KOH aqueous solution (4.0 mL, 50%), 5% Pd/C (0.032 g; 0.015 mmol of Pd), and PT agent (0.20 mmol) was magnetically stirred at 1000 rpm.

A volume of 7.0 mL of the organic solution, containing the ortho-, meta-, and para-substituted aryl halide mixture (each 0.07 M in the given solvent) and containing n-decane as internal standard, was added. Hydrogen was bubbled at atmospheric pressure in the organic phase at 1.0 mL/min.

**Hydrodechlorination of Polychlorinated Biphenyls (Aroclor 1254) with H₂ (Table 6, entries 1 and 2).** In a 25-mL three-necked round-bottomed flask thermostated with a system for the addition of hydrogen, a mixture of KOH aqueous solution (4.0 mL, 50%), 5% Pd/C (0.032 g; 0.015 mmol of Pd), and Alquat 336 (0.085 g; 0.20 mmol) was magnetically stirred at 1000 rpm. A volume of 7.0 mL of a 35 000 ppm isooctane solution (8.5 g/100 mL) of Aroclor 1254 was added and hydrogen was bubbled at atmospheric pressure in the organic phase at about 1 mL/min. n-Decane was used as internal standard. GC analysis was performed according to the following temperature program (FID detector): 140 °C, 0 min, heating rate 4 °C/min till 270 °C, stand for 10 min. The reaction products were also analyzed on the GC/MS.

**Table 6. Hydrodehalogenation of Polychlorinated Biphenyls (Aroclor 1254) with Pd/C Catalyst under Multiphase Systems**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Source of Hydrogen</th>
<th>PT Agent</th>
<th>T (°C)</th>
<th>h</th>
<th>Products (% Yields)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H₂</td>
<td>1</td>
<td>50</td>
<td>3.0</td>
<td>biphenyl (99) is the only reaction product</td>
</tr>
<tr>
<td>2</td>
<td>H₂</td>
<td>no</td>
<td>50</td>
<td>3.0</td>
<td>biphenyl (64)</td>
</tr>
<tr>
<td>3</td>
<td>Na₂HPO₄·H₂O</td>
<td>1</td>
<td>50</td>
<td>31</td>
<td>hydrodechlorination progress is about 50% biphenyl (1)</td>
</tr>
</tbody>
</table>

*For reaction conditions, see Experimental Section in Reaction of Polychlorinated Biphenyl with H₂. For reaction conditions, see Experimental Section in Reaction of Polychlorinated Biphenyls with Na₂HPO₄·H₂O, and ref 10.

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a 25-mL three-necked round-bottomed flask, a mixture of KOH aqueous solution (4.0 mL; 50%), 5% Pd/C (0.032 g; 0.015 mmol of Pd; Fluka, Art. No. 75992), (0.085 g; 0.20 mmol) of Aliquat 336 was magnetically stirred at 1000 rpm; of NaH₂PO₄·H₂O (0.20 g; 1.9 mmol) was added at the beginning and after 20 h of reaction. A volume of 7.0 mL of a 35 000 ppm isooctane solution (3.5 g/100 mL) of Aroclor 1254 was added. n-Dodecane was used as internal standard. GC analysis was performed according to the following temperature program (FID detector): 140 °C, 0 min, heating rate 4 °C/min till 270 °C, stand for 10 min. The products of reaction were analyzed with GC/MS.

Acknowledgment. This work was supported by the MURST (Ministero Università e Ricerca Scientifica e Tecnologica), Fondo 40%.

Supplementary Material Available: One figure showing hydrodehalogenation of 1,2,4,5-tetrachlorobenzene at different rates of magnetic stirring (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.