

# Effect of substituents on the hydrodechlorination reactivity of *para*-substituted chlorobenzenes

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Received 10 February 2001; accepted 17 August 2001

## Abstract

In order to determine the electronic factor affecting the hydrodechlorination reactivity of aromatic chlorinated compounds, chlorobenzene and *para*-substituted chlorobenzenes were hydrogenolyzed over a 5% Pd/C catalyst, at H<sub>2</sub> 1 MPa and 573 K. The results are discussed from the standpoints of both the energy level and the orbital coefficient of the frontier orbital using a semi-empirical calculation method.

When these chlorobenzenes were reacted, selective cleavage between the *ipso*-carbon and the chlorine atom took place and was accelerated by the presence of both electron-releasing and electron-withdrawing substituents. Between the logarithms of the reaction rate constant  $\ln(k/k_0)$  and the substitution constant  $\sigma_p^0$ , a good linear relationship for the two series was observed.

The results of the PM3 calculation of the organics suggested a good correlation in chlorobenzene reactivities with a close energy gap between the HOMO (and the LUMO) of the organics and the unoccupied part (and occupied part) of the *d*-band of the catalyst. Furthermore, the magnitude of the relative values of the HOMO coefficient on the *ipso*-carbon atom to that on the chlorine atom,  $(C_{\text{HOMO,C}})^2/(C_{\text{HOMO,Cl}})^2$ , and of the LUMO coefficient on the chlorine atom to that on the *ipso*-carbon atom,  $(C_{\text{LUMO,Cl}})^2/(C_{\text{LUMO,C}})^2$ , resulted in the same orders of reactivity for the *para*-substituted chlorobenzenes with electron-releasing and electron-withdrawing substituents. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Hydrodechlorination; *para*-Substituted chlorobenzene; Palladium carbon; Frontier orbital; Fermi level

## 1. Introduction

Since organic chlorinated compounds have commonly been used as components of pesticides, plasticizers, disinfectants, active surface agents and many other chemicals, they are nowadays widely spread in nature in the form of dust, waste and remnants [1]. Many of these organic chlorinated compounds are toxic to humans when ingested directly or indirectly. The chemical disposal of chlorinated com-

pounds is, therefore, a pressing issue for the protection of human health and the preservation of the environment.

There are several disposal methods: incineration, pyrolysis, hydrolysis, catalytic hydrogenolysis, electrolysis, biological degradation and other miscellaneous methods [2,3]. Among these, catalytic hydrogenolysis (namely, hydrodechlorination) offers greater flexibility and safety because no toxic compounds are produced in the reductive reaction conditions [3–5].

Several papers have focused on the hydrodechlorination of organic chlorinated compounds. With respect to chlorobenzene and substituted chlorobenzenes,

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for instance, the gas phase reactions over Ni/Al<sub>2</sub>O<sub>3</sub> [4,6], Ni/SiO<sub>2</sub> [7,8], Ni-Mo/Al<sub>2</sub>O<sub>3</sub> [6], Mo/Al<sub>2</sub>O<sub>3</sub> [6], Rh/Al<sub>2</sub>O<sub>3</sub> [9,10], Rh/SiO<sub>2</sub> [9], Pd/C [11], Pd/TiZrAlO<sub>x</sub> [12], Pd/TiZrSiO<sub>x</sub> [12], Pd/TiO<sub>2</sub> [12], Pd/ZrO<sub>2</sub> [12], Pd/Al<sub>2</sub>O<sub>3</sub> [10,12], Pt/Al<sub>2</sub>O<sub>3</sub> [13,14], Pt-V/Al<sub>2</sub>O<sub>3</sub> [13], Pt-Mo/Al<sub>2</sub>O<sub>3</sub> [13], Pt-W/Al<sub>2</sub>O<sub>3</sub> [13], Pt/H-BEA zeolite [14] catalyst, sulfided Ni/Al<sub>2</sub>O<sub>3</sub> [8], Ni-Mo/Al<sub>2</sub>O<sub>3</sub> [8,15], and Mo/Al<sub>2</sub>O<sub>3</sub> [8] catalyst have been studied. The liquid phase reaction over Ni/C [16], Ni-Pd/C [16], Pd/C [16,17], Pd/Al<sub>2</sub>O<sub>3</sub> [18], Pd/poly-*para*-phenyleneterephthalamide (PFT) [19], Rh/PFT [19], Rh complex [20], Pt/PFT [19], Pt/MgO-Al<sub>2</sub>O<sub>3</sub> [21], Pt/Al<sub>2</sub>O<sub>3</sub> [22], Pt/TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [22], Pt/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> [22] catalyst, sulfided Ni-Mo/Al<sub>2</sub>O<sub>3</sub> [23–25], and Co-Mo/Al<sub>2</sub>O<sub>3</sub> [25] catalyst have also been reported.

These studies provide valuable information on catalytic preparation and characterization, reaction network and reaction mechanism. However, very few studies shed light on the reactivity of aromatic chlorinated compounds [4,11].

Kraus and Bazant [11] studied the kinetics of hydrodechlorination of chlorobenzene and its derivatives over a Pd/C catalyst in a flow system, and suggested a correlation between reaction rate constants and Hammett's values. In the gaseous reaction of substituted chlorobenzenes over a supported Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, Suzdorf et al. [4] also observed a correlation between the reaction rate and the donor-properties of the substituents. The chlorobenzene substituents used in these studies, however, have been limited to a few types: amino-, hydroxyl-, methyl-, trifluoromethyl-, fluoro- and chloro-group in *ortho*-, *meta*- and/or *para*-positions. Moreover, only gaseous reaction conditions have been employed. As we aim for the practical application of hydrodechlorination, more information on the chemical properties of chlorinated compounds is needed.

Here, for the purpose of identifying the electronic factor affecting the hydrodechlorination of aromatic chlorinated compounds, chlorobenzene and six types of *para*-substituted chlorobenzenes: amino-, methoxy-, methyl-, chloro-, acetyl- and cyano-chlorobenzene, were hydrogenolyzed over a Pd/C catalyst in liquid phase. The reaction rate constants obtained were correlated with Hammett's substitution constants, and the reactivities of these *para*-substituted chlorobenzenes were discussed from the standpoints

of both the energy level and the orbital coefficient of the frontier orbital on both the *ipso*-carbon and the chlorine atom using the semi-empirical molecular orbital method PM3.

## 2. Experimental procedure

### 2.1. Materials and catalyst

Chlorobenzene and *para*-isomers of chlorotoluene, dichlorobenzene and chlorobenzonitrile were obtained from Kanto Kagaku. The *para*-isomers of chloroaniline, chloroanisole and chloroacetophenone were from Tokyo Kasei Kogyo. These materials were purified by conventional methods before use. The hexadecane and 1-methylnaphthalene used as solvents were from Aldrich and Kanto Kagaku, respectively. The hydrogen was supplied by Suzuki Shoukan. Both the solvents and the hydrogen were used without purification. The 5% Pd/C catalyst was supplied from Kawaken Fine Chemicals.

### 2.2. Apparatus

The reaction was carried out in a test tube (Pyrex, 28 mm i.d.  $\times$  65 mm height, volume ca. 77 ml), which was placed in a magnetically stirred autoclave (Sakashita Seisakusho, SUS304, volume ca. 108 ml). The autoclave was equipped with both a sampling tube (SUS316, 0.25 mm i.d.  $\times$  900 mm height) and a liquid introducing vessel (pressure-proof vessel, SUS304, volume 50 ml). At the opening of the sampling tube, 3 mg of glass wool was loaded to prevent loss of the catalyst. A diagram of the reaction system used for the present study is shown in Fig. 1.

### 2.3. Procedure and analysis

The Pd/C catalyst (0.005 g), placed into the test tube of the autoclave, was reduced in the hydrogen flow rate of 100 ml/min under 0.5 MPa at 573 K for 1 h. Upon the termination of the reductive pre-treatment of the catalyst, the residual hydrogen in the reactor was exhausted to atmospheric pressure, and hexadecane (35 ml) as major solvent was added from the

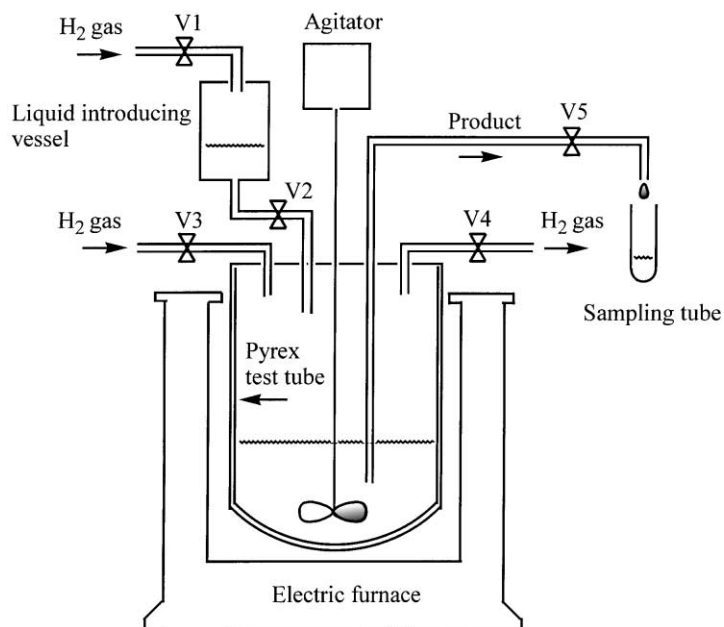


Fig. 1. Scheme of the experimental set-up (V1–V4: needle valve, V5: pressure-proof cock).

introducing vessel using 0.3 MPa hydrogen; the pressure was then adjusted to 0.5 MPa at 558 K, and the solvent and pre-treated catalyst in the vessel were stirred at 500 rpm. As soon as the temperature of the reactor attained the desired value (573 K), from the introducing vessel, reactant ( $(1.2\text{--}3.6) \times 10^{-3}$  mol) dissolved in 1-methylnaphthalene (5 ml) was added by hydrogen of ca. 0.8 MPa, following pressure adjustment to 1 MPa. During the course of the reaction, hydrogen pressure was controlled within  $\pm 0.05$  MPa using a pressure regulator (Tanaka Seisakusho, JET-S225). The reaction temperature was also controlled within  $\pm 1$  K.

When the reactant solution was introduced, the reaction time was regarded as zero. In the course of the reaction, the reaction products were taken at intervals through the sampling tube.

The products obtained were analyzed by gas chromatograph (Shimadzu 14A or B with C-R5A chromatopac) using HR-1 or HR-1701 wide bore capillary columns (Shinwa Chemical Industries Ltd., 0.56 mm i.d.  $\times$  30 m length) equipped with temperature programming functions and a fire ionization detector. Identification was carried out by comparing

the retention time of the product with that of the authentic sample. In the quantitative analysis, toluene, *meta*-xylene or 1,3,5-trimethylbenzene was used as the inner standard sample.

#### 2.4. Data analysis and molecular orbital calculations

The initial reaction rates were determined by the plotting of the concentration of the dechlorinated product versus reaction time. As approximate method, power series within the third order ( $at^3 + bt^2 + ct$ ) were applied to the plotted data, and the initial reaction rate was determined as the differential coefficient of the power series at  $t = 0$ , that is the coefficient of the first order term.

Calculations by the semi-empirical PM3 method based on the restricted Hartree-Fock (RHF) method were carried out using WinMOPAC Version 3.2 (Fujitsu) running on the Windows 95 system. The starting geometries of the chlorobenzenes were constructed using the program included in the WinMOPAC. The geometric optimization was terminated when the RMS gradient fell below 0.05 (default value).

### 3. Results and discussion

#### 3.1. Hydrodechlorination

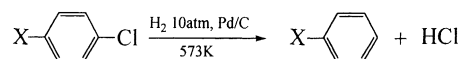
##### 3.1.1. Chlorobenzene

In the hydrodechlorination of chlorobenzene over a 5% Pd/C catalyst at 573 K, benzene was formed selectively, and none of the aliphatic compounds were produced in detectable amounts. As shown in Figs. 2 and 3, the reaction rate of the benzene formation was proportional to the initial concentration of chlorobenzene, with an approximate order of 0.90. Furthermore, with respect to hydrogen pressure, the reaction order was approximately 0.52.

##### 3.1.2. *para*-Substituted chlorobenzenes

In order to verify the electronic effect of the substituents on the hydrodechlorination of the aromatic chlorinated compounds, a series of *para*-substituted chlorobenzenes with electron-releasing or electron-withdrawing substituents were hydrogenolyzed under the same reaction conditions as those of chlorobenzene.

In the reaction of the *para*-isomers of chloroaniline, chloroanisole and chlorotoluene, which possess electron-releasing substituents, aniline, anisole and toluene were formed, respectively. Also, in the case of the *para*-isomers of dichlorobenzene, chloroacetophenone and chlorobenzonitrile, which possess electron-withdrawing substituents, chlorobenzene, acetophenone and benzonitrile were observed as respective products. As shown in the following reaction formula, such product distributions indicate that selec-



tive reductive cleavage between the *ipso*-carbon and the chlorine atom took place. With respect to the initial concentration of each reactant, the reaction orders were in the range of about 0.91–0.99 (results shown in Figs. 2 and 3.)

When we compared the reaction rate constants of these *para*-substituted chlorobenzenes, the following orders were observed: chloroaniline > chloroanisole > chlorotoluene > chlorobenzene, and chlorobenzonitrile > chloroacetophenone >

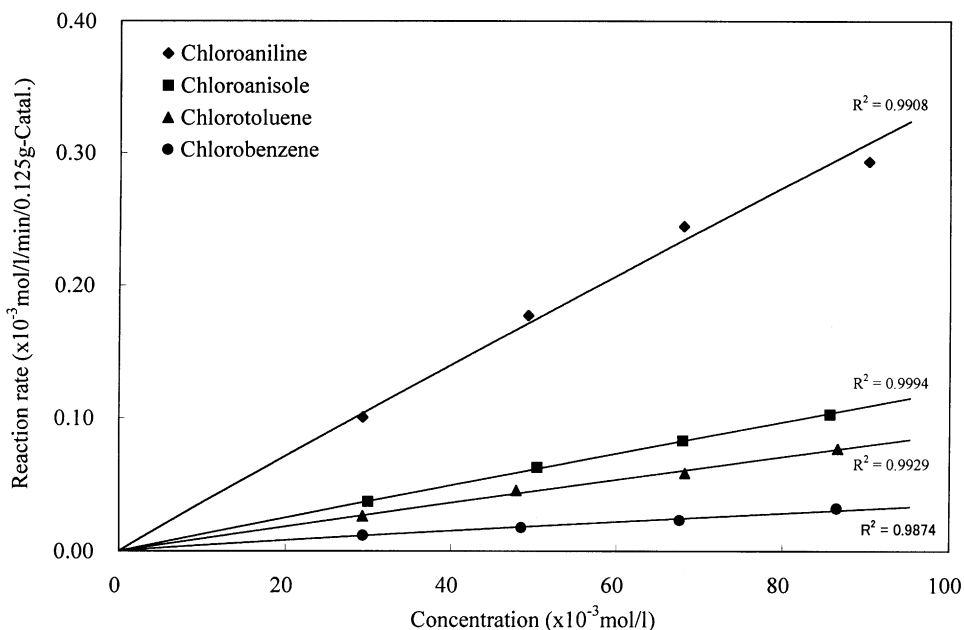


Fig. 2. Reaction rates of chlorobenzene and the *para*-isomers of chloroaniline, chloroanisole and chlorotoluene in the hydrodechlorination over 5% Pd/C catalyst at H<sub>2</sub> 1 MPa and 573 K.

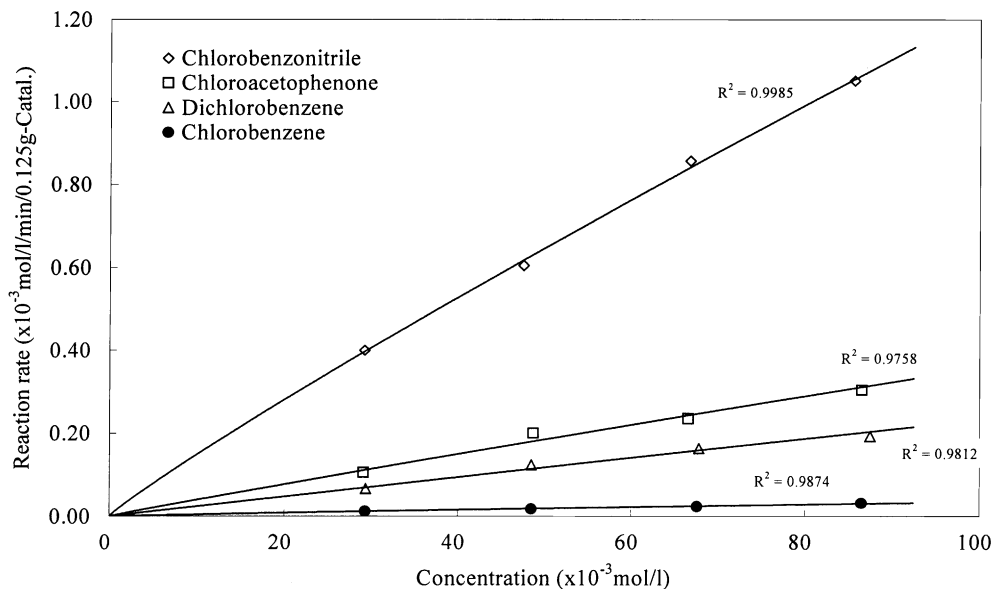


Fig. 3. Reaction rates of chlorobenzene and the *para*-isomers of chlorobenzonitrile, chloroacetophenone and dichlorobenzene in the hydrodechlorination over 5% Pd/C catalyst at H<sub>2</sub> 1 MPa and 573 K.

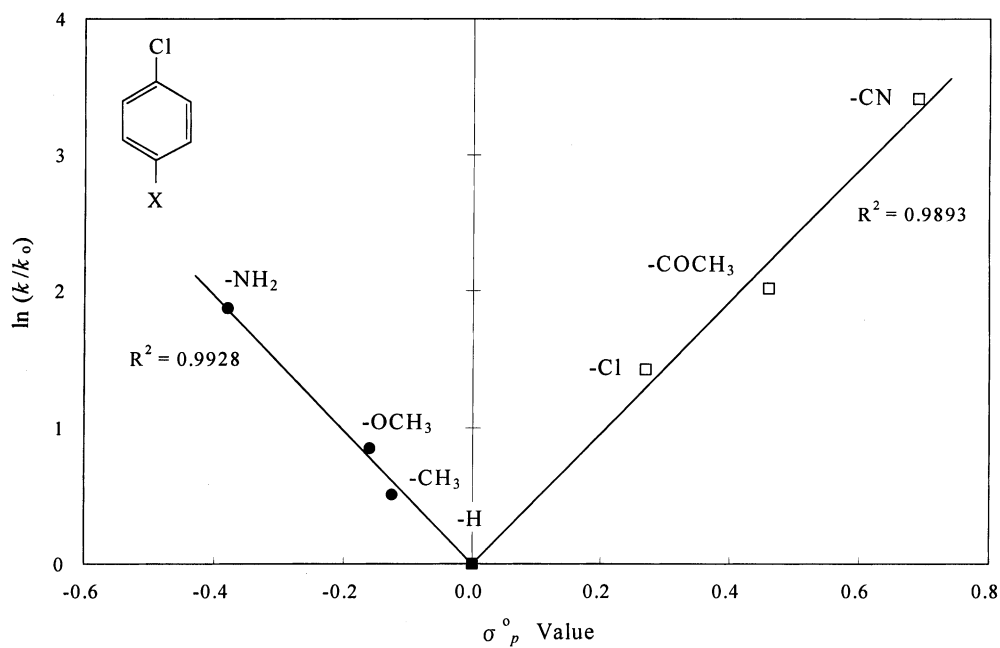


Fig. 4. Plots of the logarithms of reaction rate constant  $\ln(k/k_0)$  to  $\sigma_p^0$  value.

dichlorobenzene > chlorobenzene. These results indicate that the reactivities of the *para*-substituted chlorobenzenes over Pd/C catalyst are accelerated by the presence of both electron-releasing and electron-withdrawing substituents.

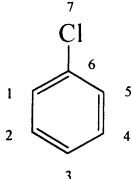
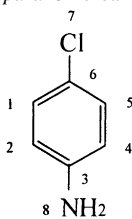
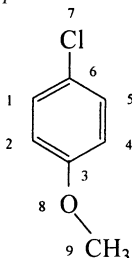
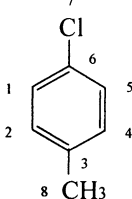
Furthermore, when the reaction rates were regarded as to be in proportional to the catalytic amount, interesting results were obtained in the quantitative evaluation [26] of these substituent effects. In fact, between the logarithms of the reaction rate constant  $\ln(k/k_0)$ , where  $k$  is the reaction rate constant of the substituted

chlorobenzenes and  $k_0$  that of chlorobenzene, and the substitution constants  $\sigma_p^0$  [27,28], good linear relationships divided into two series were observed (the correlation coefficient square  $R^2$  for the electron-releasing group and the electron-withdrawing group is 0.9928 and 0.9893, respectively.) These results are shown in Fig. 4.

Note that the reaction parameter  $\rho$  of the electron-releasing and the electron-withdrawing groups is  $-4.91$  and  $4.82$ , respectively. The negative  $\rho$  value suggests that the hydrodechlorination of

Table 1

Geometries of chlorobenzene and the *para*-isomers of chloroaniline, chloroanisole and chlorotoluene used for the PM3 calculation

	Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
<b>Chlorobenzene</b>						
	C1–C2	1.390	C1–C2–C3	120.2	C1–C2–C3–C4	0.0
	C2–C3	1.392	C2–C3–C4	120.2	C2–C3–C4–C5	0.0
	C3–C4	1.392	C3–C4–C5	120.2	C3–C4–C5–C6	0.0
	C4–C5	1.390	C4–C5–C6	119.3	C4–C5–C6–C1	0.0
	C5–C6	1.393				
	C17–C6	1.686	C17–C6–C5	119.5	C17–C6–C5–C4	180.0
<b><i>para</i>-Chloroaniline</b>						
	C1–C2	1.388	C1–C2–C3	119.9	C1–C2–C3–C4	-0.3
	C2–C3	1.403	C2–C3–C4	119.9	C2–C3–C4–C5	0.3
	C3–C4	1.403	C3–C4–C5	119.9	C3–C4–C5–C6	-0.2
	C4–C5	1.388	C4–C5–C6	119.7	C4–C5–C6–C1	-179.9
	C5–C6	1.393	C5–C6–C17	119.6	C5–C6–C17–C8	174.9
	C6–C17	1.687	C6–C17–C8	120.0		
	C3–N8	1.428				
<b><i>para</i>-Chloroanisole</b>						
	C1–C2	1.391	C1–C2–C3	119.3	C1–C2–C3–C4	0.0
	C2–C3	1.399	C2–C3–C4	120.8	C2–C3–C4–C5	0.0
	C3–C4	1.406	C3–C4–C5	119.4	C3–C4–C5–C6	0.0
	C4–C5	1.386	C4–C5–C6	119.7	C4–C5–C6–C1	180.0
	C5–C6	1.395	C5–C6–C17	119.4	C5–C6–C17–O8	180.0
	C6–C17	1.687	C6–C17–O8	125.4	C6–C17–O8–C9	0.0
	C3–O8	1.380	C3–O8–C9	117.5		
	O8–C9	1.406				
<b><i>para</i>-Chlorotoluene</b>						
	C1–C2	1.388	C1–C2–C3	120.4	C1–C2–C3–C4	0.0
	C2–C3	1.398	C2–C3–C4	119.6	C2–C3–C4–C5	0.0
	C3–C4	1.396	C3–C4–C5	120.3	C3–C4–C5–C6	0.0
	C4–C5	1.390	C4–C5–C6	119.4	C4–C5–C6–C1	180.0
	C5–C6	1.392	C5–C6–C17	119.6	C5–C6–C17–C8	180.0
	C6–C17	1.686	C6–C17–C8	119.6		
	C3–C8	1.485				

the *para*-substituted chlorobenzenes possessing electron-releasing substituents is an electrophilic reaction at the reaction center. The same reactivity trend was reported for the *para*-isomers of chloroaniline, chlorophenol and chlorotoluene over Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst [4] in the gas phase reaction. For the *para*-substituted chlorobenzenes possessing electron-withdrawing substituents, on the other hand, the positive  $\rho$  value indicates an electron deficiency at the reaction center. This reactivity behavior is the same as that of Kraus and Bazant [11], in which the *meta*-isomers of chlorotrifluoromethylbenzene, dichlorobenzene and chlorofluorobenzene were reacted over a 0.3% Pd/C catalyst in gas phase conditions. In the case of the reaction of *para*- and *meta*-dichlorobenzene and

*para*-chlorotrifluoromethylbenzene over a Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst [4], however, the opposite reactivity tendency was reported. Such difference might be attributed mainly to the catalytic properties. In the next section, we will try to clarify the factors affecting reactivity from the standpoint of the frontier molecular orbital method.

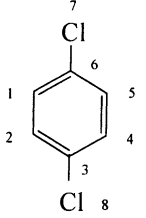
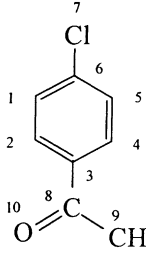
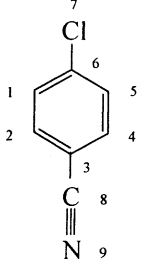
### 3.2. Molecular orbital calculation

#### 3.2.1. HOMO and LUMO energy levels

A few studies on the hydrodechlorination of chlorobenzenes over metal catalyst have suggested a weak bond formation between the chlorine atom and the metal surface [7,10,11,21]. Furthermore, in the present investigation, the values of the reaction

Table 2

Geometries of the *para*-isomers of dichlorobenzene, chloroacetophenone and chlorobenzonitrile used for the PM3 calculation

	Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
<i>para</i> -Dichlorobenzene						
	C1–C2	1.390	C1–C2–C3	119.5	C1–C2–C3–C4	0.0
	C2–C3	1.394	C2–C3–C4	121.1	C2–C3–C4–C5	0.0
	C3–C4	1.394	C3–C4–C5	119.5	C3–C4–C5–C6	0.0
	C4–C5	1.390	C4–C5–C6	119.5	C1–C2–C3–Cl8	180.0
	C5–C6	1.394	C2–C3–Cl8	119.5	C1–C2–C3–Cl8	180.0
	C3–Cl8	1.685	C5–C6–Cl7	119.5	C4–C5–C6–Cl7	180.0
	C6–Cl7	1.685				
<i>para</i> -Chloroacetophenone						
	C1–C2	1.389	C1–C2–C3	120.6	C1–C2–C3–C4	0.0
	C2–C3	1.398	C2–C3–C4	119.1	C2–C3–C4–C5	0.0
	C3–C4	1.399	C3–C4–C5	120.6	C3–C4–C5–C6	0.0
	C4–C5	1.390	C4–C5–C6	119.5	C4–C5–C6–C17	–180.0
	C5–C6	1.392	C5–C6–C17	119.7	C1–C2–C3–C8	–180.0
	C6–C17	1.683	C2–C3–C8	121.5	C2–C3–C8–C9	0.0
	C3–C8	1.494	C3–C8–C9	118.2	C2–C3–C8–O10	180.0
	C8–C9	1.507	C3–C8–O10	121.2		
	C8–O10	1.219				
<i>para</i> -Chlorobenzonitrile						
	C1–C2	1.389	C1–C2–C3	119.5	C1–C2–C3–C4	0.0
	C2–C3	1.398	C2–C3–C4	120.8	C2–C3–C4–C5	0.0
	C3–C4	1.398	C3–C4–C5	119.5	C3–C4–C5–C6	0.0
	C4–C5	1.389	C4–C5–C6	119.6	C4–C5–C6–C17	180.0
	C5–C6	1.394	C5–C6–C17	119.5	C1–C2–C3–C8	180.0
	C6–C17	1.682	C2–C3–C8	119.6	C1–C2–C3–C8	180.0
	C3–C8	1.425	C3–C8–N9	180.0	C2–C3–C8–N9	–180.0
	C3–C8	1.425				
	C8–N9	1.160				

parameters of both the electron-releasing and the electron-withdrawing substituents ( $\rho = -4.91$  and  $4.82$ , respectively) allow us to suspect the participation of the HOMO and the LUMO in the reaction.

According to the PM3 calculation of chlorobenzenes, whose molecular structures are shown in Tables 1 and 2, the HOMO and the LUMO of all chlorobenzenes are  $\pi$ -molecular orbitals. The energy level results of these HOMO and LUMO are shown in Fig. 5.

As for the *para*-substituted chlorobenzenes with electron-releasing substituents, when the Fermi level of the Pd/C catalyst is regarded as located between the HOMO and the LUMO levels of the chlorobenzenes, the energy gap degree between the HOMO of the chlorobenzenes and the unoccupied part in the energy band (i.e. *d*-band) of the catalyst is increased in the opposite order of reactivity. It is well known that a smaller energy gap between the HOMO of one reactant and the LUMO of another reactant gives rise to a larger HOMO–LUMO interaction [29,30]. In the present study, therefore, the magnitude of interaction between the chlorine atom of the organics and the catalytic surface is expected to decrease in the order of chloroaniline > chloroanisole > chlorotoluene >

chlorobenzene, which is in good agreement with the experimental reactivity results. This energy correlation behavior is illustrated in Fig. 6. Thus, the HOMO of the chlorobenzenes might be interacting with the bottom of the unoccupied part in the *d*-band of the Pd/C catalyst [31].

In the case of the *para*-substituted chlorobenzenes with electron-withdrawing substituents, as mentioned above, the role of the LUMO of the organics is important in the reaction. If the Fermi level of the Pd/C catalyst is located between the HOMO and LUMO levels of the chlorobenzenes, as seen in Fig. 7, the degree of the energy gap between the top of the occupied part in the *d*-band of the Pd/C catalyst and the LUMO of the chlorobenzenes is increased in the opposite order of reactivity. Since a smaller energy gap causes a larger HOMO–LUMO interaction in general, the degree of interaction of the chlorine atom with the catalytic surface is expected to decrease in the following order: chlorobenzonitrile > chloroacetophenone > dichlorobenzene > chlorobenzene, thereby leading the reaction to proceed in the same order. This predicted order is also consistent with the order obtained experimentally.

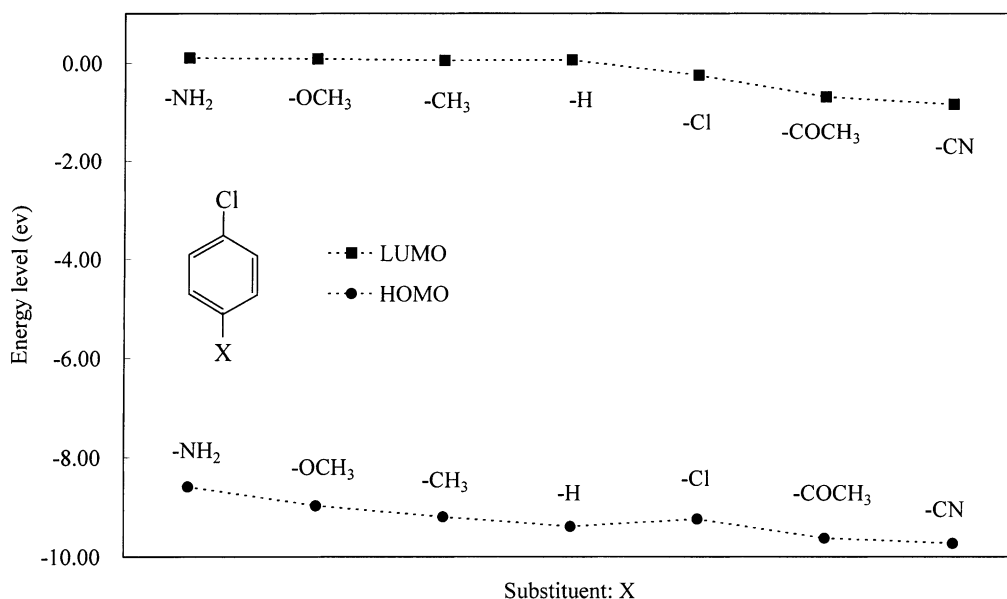


Fig. 5. Energy levels of HOMO and LUMO of the *para*-substituted chlorobenzenes by PM3 method.



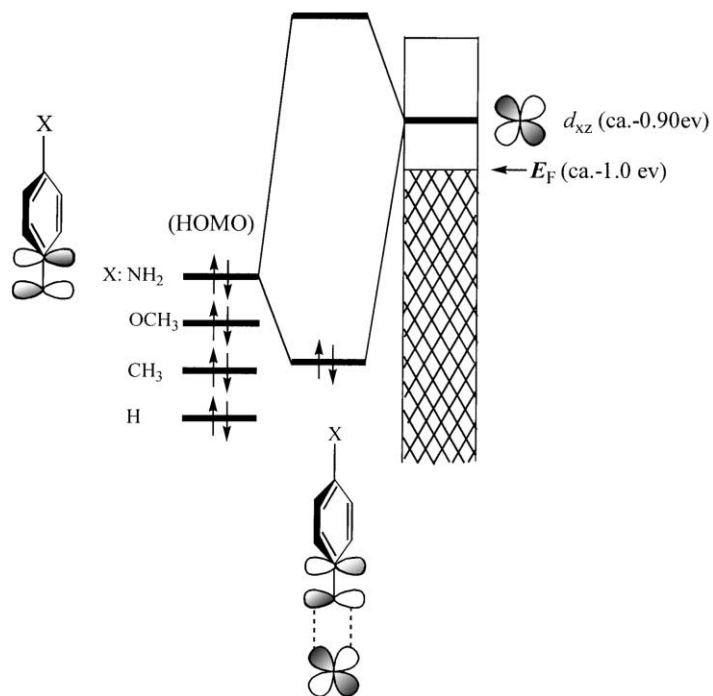


Fig. 6. Energy correlation of HOMO of chlorobenzenes and unoccupied part of metal  $d_{xz}$ -band.

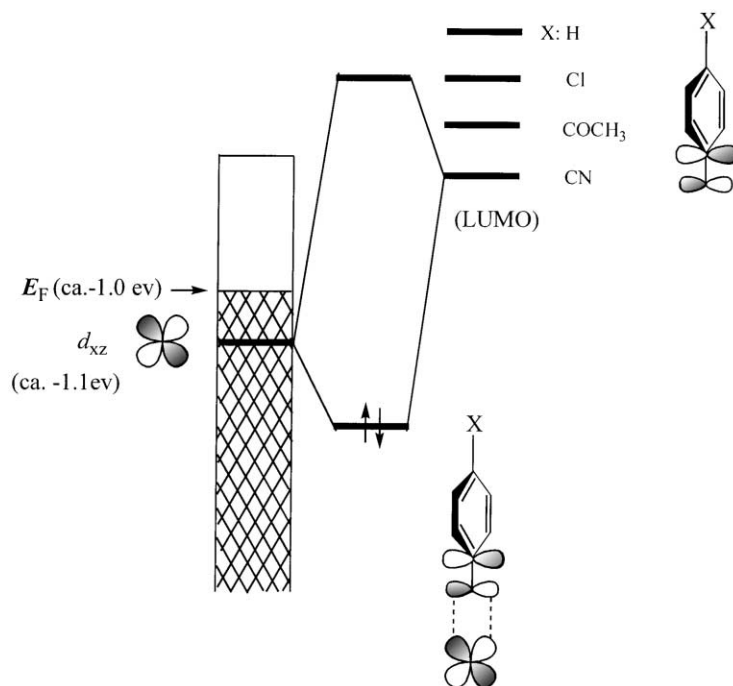
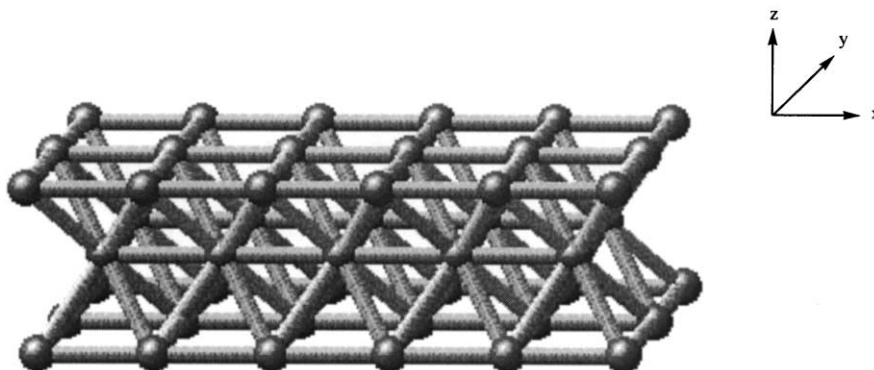


Fig. 7. Energy correlation of LUMO of chlorobenzenes and occupied part of metal  $d_{xz}$ -band.

Table 3

Energy levels of HOMO and LUMO of chlorobenzenes and Fermi level of Pd<sub>48</sub> cluster by DV-X $\alpha$  method

Substituent X in Cl-C <sub>6</sub> H <sub>4</sub> -X	NH <sub>2</sub>	OCH <sub>3</sub>	CH <sub>3</sub>	H	Cl	COCH <sub>3</sub>	CN	Cluster
HOMO (eV)	-1.606	-1.666	-2.284	-2.447				
Fermi level (eV)								ca. -1.0
LUMO (eV)				2.742	2.152	1.161	1.471	

Fig. 8. Structure of Pd<sub>48</sub> cluster (fcc) used for the preliminary DV-X $\alpha$  calculation.

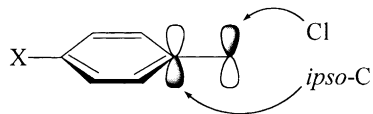
In the preliminary calculation using DV-X $\alpha$  [32] method based on the density functional theory, as shown in Table 3, the order of the energy level of both the HOMO and the LUMO of chlorobenzenes are similar to that of PM3 though the absolute values are different from the PM3. When Pd<sub>48</sub> (fcc,  $a = 3.89 \text{ \AA}$ ) shown in Fig. 8 is used as a model cluster, the Fermi level is situated favorably between the HOMO and the LUMO, and the  $d_{xz}$  orbital is observed both in the bottom of the unoccupied part and the top of

the occupied part of metal  $d$ -band. Although further investigation is required in order to clear the orbital interaction, this orbital may be related to the adsorption of the chlorobenzenes. Such feature is also illustrated both in Figs. 6 and 7.

### 3.2.2. HOMO and LUMO coefficients

Along with the energy level, the coefficient of the frontier molecular orbital on the atom of reaction center may also be an important factor affecting reactivity.

Table 4

Coefficients of HOMO and LUMO both on *ipso*-carbon and chlorine atom of chlorobenzene and the *para*-substituted chlorobenzenes

Substituent X in Cl-C <sub>6</sub> H <sub>4</sub> -X	NH <sub>2</sub>	OCH <sub>3</sub>	CH <sub>3</sub>	H	Cl	COCH <sub>3</sub>	CN
Coefficient of HOMO							
On <i>ipso</i> -carbon atom	0.417	0.456	-0.446	-0.439	-0.412	-0.416	-0.413
On chlorine atom	-0.363	-0.474	0.536	0.593	0.467	0.594	0.577
Coefficient of LUMO							
On <i>ipso</i> -carbon atom	0.549	0.272	0.567	0.580	0.566	0.507	-0.529
On chlorine atom	-0.122	-0.060	-0.128	-0.130	-0.131	-0.125	0.131

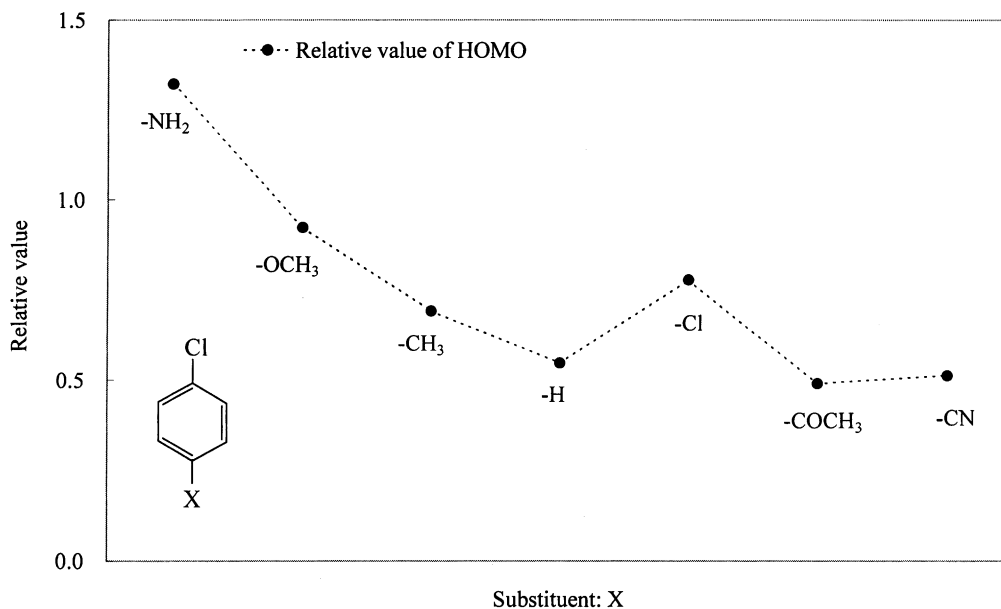


Fig. 9. Relative values of the coefficient of HOMO on carbon atom to that on chlorine atom,  $(C_{\text{HOMO,C}})^2 / (C_{\text{HOMO,Cl}})^2$ .

Therefore, the HOMO and LUMO coefficients on the *ipso*-carbon and the chlorine atom were measured by the PM3 method, and the results are shown in Table 4.

In this table, all of the HOMO and LUMO are  $\pi$ -molecular orbitals. In the case of the *para*-substituted chlorobenzene with electron-releasing substituents, as mentioned above, the HOMO is expected to play

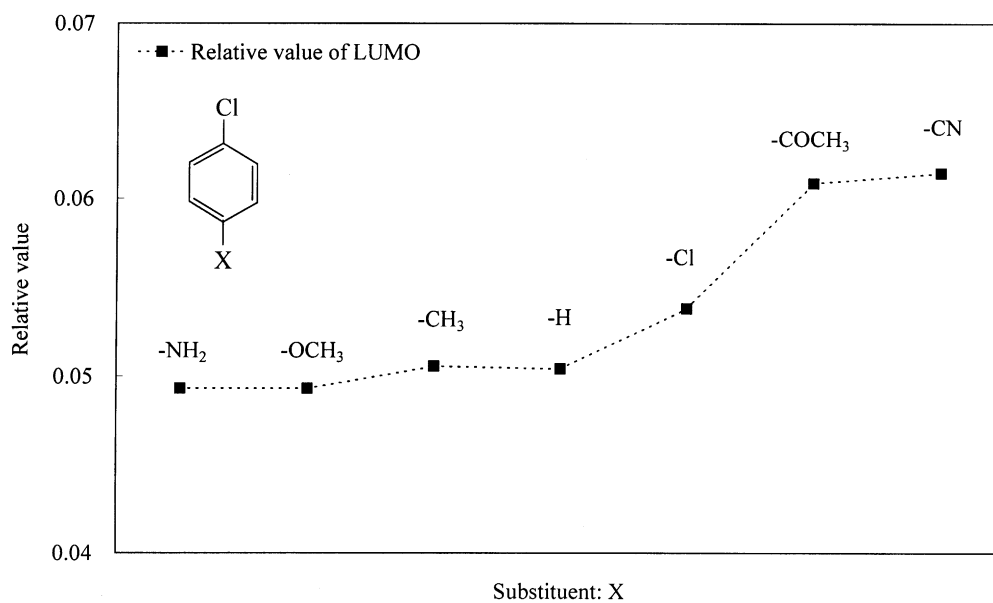


Fig. 10. Relative values of the coefficient of LUMO on chlorine atom to that on carbon atom,  $(C_{\text{LUMO,Cl}})^2 / (C_{\text{LUMO,C}})^2$ .

a more important role than the LUMO. From the coefficients in Table 4, we can infer that all of the HOMO spread widely both on the *ipso*-carbon and the chlorine atom with different phases. Although regularity is observed in the order of magnitude of the coefficient on the chlorine atom, no direct relationship between coefficient and hydrodechlorination reactivity is observed in the other coefficients.

For the *para*-substituted chlorobenzenes with electron-releasing substituents, on the other hand, the relative value of the HOMO coefficient (namely, frontier electron density) on the *ipso*-carbon atom to that on the chlorine atom,  $(C_{\text{HOMO,C}})^2/(C_{\text{HOMO,Cl}})^2$ , resulted in the same order of reactivity. In the case of the *para*-substituted chlorobenzenes with electron-withdrawing substituents, the relative value of the LUMO coefficient on the chlorine atom to that on the *ipso*-carbon atom,  $(C_{\text{LUMO,Cl}})^2/(C_{\text{LUMO,C}})^2$ , also resulted in the same order of reactivity. These results are shown in Figs. 9 and 10. Similar results in relative value were observed in the hydrodesulfurization of *para*-substituted benzenethiols [33]. Although the theoretical background is not clear, these values might serve as useful reaction indices.

#### 4. Conclusion

1. The hydrodechlorination of *para*-substituted chlorobenzenes over a 5% Pd/C catalyst is accelerated by the presence of both electron-releasing and electron-withdrawing substituents.
2. Between the logarithms of the reaction constant  $\ln(k/k_0)$  and the substitution constant  $\sigma_p^0$  linear relationships are observed. Furthermore, for the substituted chlorobenzenes with electron-releasing and electron-withdrawing substituents, the reaction parameter  $\rho$  is  $-4.91$  and  $4.82$ , respectively.
3. According to PM3 calculations, the reactivities of the chlorobenzenes seem to correlate with the closeness of the energy gap between the HOMO (and LUMO) of the organics and the unoccupied part (and occupied part) of the *d*-band of the catalyst, located in the neighborhood of the Fermi level.
4. The relative values of the HOMO coefficient on the *ipso*-carbon atom to that on the chlorine atom,  $(C_{\text{HOMO,C}})^2/(C_{\text{HOMO,Cl}})^2$  and of the

LUMO coefficient on the chlorine atom to that on the *ipso*-carbon atom  $(C_{\text{LUMO,C}})^2/(C_{\text{LUMO,Cl}})^2$ , resulted in the same orders of reactivity. These relative values may be useful indicators of reactivity.

#### Acknowledgements

The authors gratefully acknowledge Dr. Seiichi Takase for his guidance on the molecular orbital theory. We are also appreciative of the experimental assistance of Miss Yuki Hasegawa.

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