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Dechlorination of Polychlorobenzenes over Triiron Tetraoxide in the Presence of Hydrogen Donating Solvents

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Dechlorination of polychlorobenzenes over Fe_3O_4 was investigated by a pulse micro-reactor technique. Dechlorinations of various polychlorobenzenes in hexane and cyclohexane were carried out in the gas phase at the temperatures ranging from 498 to 623 K. In the presence of such hydrogen donating solvents, dechlorination was shown to proceed almost exclusively. The relative rates of dechlorination were measured by gas chromatography. It was found that the solvents used to dissolve polychlorobenzenes plays a role of a hydrogen donor in this reaction. The different rates among unequivalent chlorine atoms in a molecule were interpreted by the effect of steric acceleration caused by the neighboring chlorine atom(s). The reaction will probably proceed *via* hydrogenolytic cleavage of C–Cl bonds.

Recently, environmental contamination with polyhalogenated aromatic compounds has been a serious problem in many countries. For the first time, poisoning caused by polychlorinated biphenyls attracted the public attention, which stimulated the investigations on physical and biological properties, as well as chemical reactions, of other polyhalogenated aromatics.1) Considerably large number of researches concerning their occurrence in environment, hazard, toxicity, and metabolism were reported.2) And dehalogenation of polyhalogenated aromatic compounds have been investigated rather extensively in the view point of their detoxication. In this respect, several photochemical dehalogenation procedures have been reported in this decade.3,4) However, the chemical behaviors of polyhalobenzenes have not been studied so extensively as polychlorobiphenyls.

In our previous reports, thermal decomposition of tribromobenzenes5) and photochemical dehalogenation of polyhalobenzenes in hexane solution6) were surveyed and their mechanism was discussed. From these experiments, the reactivities of halogen (Cl or Br) atoms occupying different positions were interpreted in terms of steric acceleration. In this paper, the authors wish to report an efficient method for the dechlorination of polychlorobenzenes by Fe_3O_4 in the presence of hexane or cyclohexane.

Experimental

Materials. Triiron tetraoxide (Fe_3O_4) was prepared by hydrolyzing a 1:1 (molar ratio) mixture of iron(II) and iron(III) chlorides with urea in aqueous solution. Under these conditions, fine particles of Fe_3O_4 were produced, their average size being determined to be 8.0 nm in diameter from the line broadening of the powder X-ray diffraction lines.

Some of polychlorobenzenes used in this investigation were prepared by a combination of direct halogenation and nitration followed by reduction and the Sandmeyer reaction (replacement by Cl) of appropriately halogenated benzenes and anilines. Commercially available materials were used after purification by distillation or by chromatography. All of polychlorobenzenes were identified by their melting and/or boiling points and by spectral properties.

Reactions. Dechlorination of polychlorobenzenes over Fe_3O_4 was carried out in a stream of helium as a carrier gas by use of a pulse micro-reactor technique in combination with gas chromatography for analysis.7) The products and the residual reactant were determined quantitatively by means of gas chromatography. Gas chromatographic analyses were carried out on a Shimadzu GC-4B PFT apparatus equipped with a PEG 20 M column (glass, 3 mm×2 m). Details of the apparatus for the reactions were described in our previous paper.8) The hexane or cyclohexane solution of polychlorobenzene was injected in portions (each 1.0 μl) to the reaction chamber containing 550 mg of Fe_3O_4.

Results and Discussion

Dehalogenation Activity and Activation of Fe_3O_4 by Hydrogen Donating Solvents. Newly prepared Fe_3O_4 is inactive towards dechlorination of polychlorobenzenes. For this reason, a pretreatment procedure was contrived in order to activate the new Fe_3O_4. While we are investigating the dechlorination in hexane solution, the treatment by hexane was shown to be effective for the activation of Fe_3O_4 by chance. And the dechlorination proceeded smoothly when a hexane solution of polychlorobenzene was injected to the reaction column containing pretreated Fe_3O_4. By the further examination with various solvents, Fe_3O_4 was shown to be activated by the pretreatment with hydrogen donating solvents, such as hexane, cyclohexane, and tetraline. Reactivity of Fe_3O_4 towards dehalogenation was influenced considerably by the nature and the amount of the hydrogen donor used for the pretreatment.9)

Figure 1 shows the reactivity of Fe_3O_4 as a function of the amount of hexane used for the pretreatment. In this figure, the ordinate is scaled by an arbitrary unit proportional to the amount of the dechlorination product of 1,2,3-trichlorobenzene used as a probe for the reactivity towards dechlorination. In the process of the pretreatment, hydrogen was thought to be supplied to the surface of Fe_3O_4 from the hydrogen donating solvent. The hydrogen uptake of Fe_3O_4 was proven by the fact that a small amount of benzene was detected

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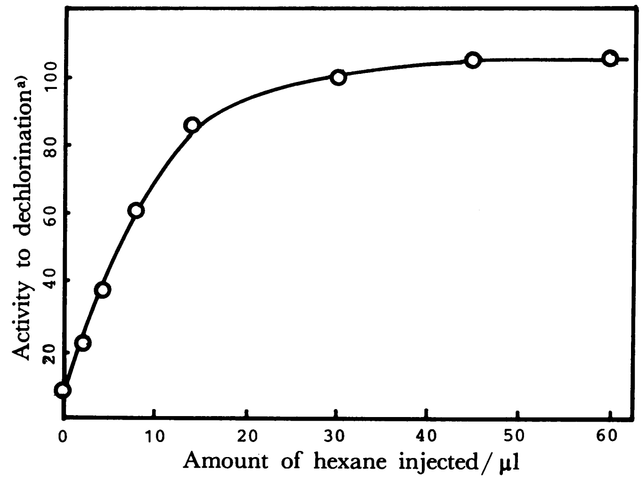

Fig. 1. Effect of the amount of hexane used for the pretreatment on the activity of Fe_3O_4 at 623 K (Amount of Fe_3O_4; 13.8 mg.

during the pretreatment of Fe_3O_4 by cyclohexane at 623 K. Since gaseous hydrogen reduces Fe_3O_4 to metallic iron under similar conditions,[10] the surface of Fe_3O_4 might be partly be reduced to Fe(0) during the pretreatment. In the case shown in Fig. 1, the Fe_3O_4 system seemed to have reached to an equilibrium after the pretreatment by 60 μl of hexane (as can be deduced from the plateau of the reactivity *vs.* the amount of hydrogen donor curve in this figure). The pretreated Fe_3O_4 showed the diffraction lines of original Fe_3O_4 in its powder X-ray spectrum, however.

Fe_3O_4 could be activated more effectively by use of a hydrogen donor stronger than hexane. Thus, Fe_3O_4 activated by 1,2,3,4-tetrahydronaphthalene (tetraline) is more reactive towards dechlorination. Naphthalene was detected as a product on passing tetraline over Fe_3O_4, rendering another support for the dehydrogenation on the surface of Fe_3O_4. On the other hand, benzene is little effective for the activation, and Fe_3O_4 shows no activity even after passing a considerable amount of benzene over the newly prepared Fe_3O_4. During the process of pretreatment by hydrogen donor, the color of Fe_3O_4 powder changed from dark brown to dark grey getting still darker after used for dechlorination.

Dechlorination of Polychlorobenzenes over Fe_3O_4. The dechlorination was carried out at first with the hexane solution of polychlorobenzene at 623 K, where the vaporized solvent played a part of hydrogen donor in the reaction, by use of the fine powder of Fe_3O_4 (550 mg) prepared as described in the experimental section and pretreated by 500 μl of hexane. Further pretreatment did not improve the activity to a measurable extent. The results are summarized in Table 1.

We have already correlated the migrating ability of the halogen atoms of polyhalobenzenes with the steric and the electronic factors during the Jacobsen type rearrangement[11] and also during the photo-dehalo-

TABLE 1. DECHLORINATION OF VARIOUS POLYCHLOROBENZENES OVER Fe_3O_4 IN THE PRESENCE OF HYDROGEN DONATING SUBSTANCE$^{a)}$

Substrate$^{b)}$	Solvent$^{d)}$	Conversion	Produced (poly)chlorobenzenes/%										
		%	none	mono	ortho	meta	para	1,2,3	1,2,4	1,3,5	1,2,3,4	1,2,3,5	1,2,4,5
C_6H_5Cl	h	59.2	59.2	40.8									
	ch	58.3	58.3	41.7									
o-$C_6H_4Cl_2$	h	80.6	47.0	33.6	19.4								
	ch	78.9	46.0	32.9	21.1								
m-$C_6H_4Cl_2$	h	19.7	11.5	8.2		80.3							
	ch	13.8	8.1	5.8		86.1							
p-$C_6H_4Cl_2$	h	19.7	11.5	8.2			80.3						
	ch	13.1	7.7	5.4			86.9						
$C_6H_3Cl_3$	h	88.2	28.2	20.3	16.3	23.4		11.8					
(1,2,3)	ch	90.2	30.4	21.7	16.2	22.0		9.8					
$C_6H_3Cl_3$	h	70.6	6.9	15.5	0.9	29.5	27.8		29.4				
(1,2,4)	ch	74.2	11.4	8.1	2.3	27.1	25.3		25.8				
$C_6H_3Cl_3$	h	13.6	0.8	0.6		12.2				86.4			
(1,3,5)	ch	13.8	trace	trace		13.8				86.2			
$C_6H_2Cl_4$	h	96.2	12.0	8.4	9.8	24.5	14.1	6.4	21.0		3.8		
(1,2,3,4)	ch	94.7	14.9	10.7	8.2	20.6	11.4	6.3	22.6		5.3		
$C_6H_2Cl_4$	h	80.0	3.4	3.0	trace	12.5	6.0	0.4	21.7	33.0		20.0	
(1,2,3,5)	ch	87.1	5.0	3.6	0.8	16.6	11.9		18.9	30.3		12.9	
$C_6H_2Cl_4$$^{c)}$	h	79.3	3.5	2.4		19.1	18.5		35.8				20.7
(1,2,4,5)	ch	81.5	4.0	2.8		20.4	19.9		34.4				18.5
$C_6HCl_5$$^{c)}$	h	98.0	4.8	3.0	trace	18.2	14.9		28.4	12.7		18.0	
	ch	97.2	5.6	4.3	trace	18.8	14.7		27.3	12.1		17.2	
$C_6Cl_6$$^{c)}$	ch	100.0				13.8	15.1	2.8	48.0	20.3			

a) 550 mg of Fe_3O_4 was used after pretreatment with 500 μl of hexane or cyclohexane. b) A 1.0 μl portion of the hexane or the cylohexane solution of the substrate (concn., 1.0 mol/l) was injected at a time. c) Saturated solution. d) h and ch refer hexane and cyclohexane, respectively.

genation.6) In connection with these previous studies, we have paid much attention on the effect of the number and the positions of chlorine atoms on their reactivities, *i. e.*, the ease of removal. In this series of experiments with Fe_3O_4, the polychlorobenzene tends to be more reactive in the following order: 1,3,5-trichloro<1,4-dichloro<1,3-dichloro<monochloro<1,2,4-trichloro<1,2-dichloro<1,2,3,5-tetrachloro<1,2,3-trichloro<1,2,3,4-tetrachloro<pentachloro<hexachloro derivative. In general, the dechlorination becomes easy with the increase in the steric hindrance caused by the neighboring chlorine atoms and also by the buttressing effect12) of the next neighbor chlorine atoms. Additional isolated halogen atom(s) on the ring tend to deactivate the dechlorination reaction as evidenced by the first four compounds of the above sequence. In other words, hexachlorobenzene is the most reactive, and the reactivity decreases in the following order: Polychlorobenzene having five adjacent Cl atoms> that having four adjacent Cl atoms>those having three adjacent Cl atoms>those having two adjacent Cl atoms>those having isolated Cl atom(s) only. For example, 1,2,3-trichlorobenzene is the most reactive and 1,3,5-trichloro derivative the least reactive among isomeric trichlorobenzenes. When compared intramolecularly, the most crowded chlorine atom tends to be eliminated most easily. Thus the dechlorination of 1,2,3-trichlorobenzene gives *m*-dichlorobenzene most predominantly by the elimination of the most hindered 2-chlorine atom. Similarly, 1,2,4-trichlorobenzene is the most predominant product by the dechlorination of 1,2,3,4-tetrachlorobenzene. The results are very similar to the photochemical dechlorination of polychlorobenzenes in hexane.6) Hydrogen chloride was not detected as a gaseous product in any runs carried out over the newly pretreated Fe_3O_4.9) When cyclohexane was used as a solvent, nearly the same results as in hexane were obtained.

Dechlorinations of trichlorobenzene isomers dissolved in hexane and cyclohexane were carried out over Fe_3O_4 in the temperature range of 498—623 K in order to examine the dependence on temperature. The temperature affected the products of the reaction in a very similar way when hexane and cyclohexane solutions were dechlorinated. Thus, only the results on their hexane solutions are illustrated in Fig. 2 as a typical example. In these runs, Fe_3O_4 was again pretreated by 500 μl of cyclohexane. The difference in the reactivity among the positional isomers is mainly determined by the circumstances of chlorine atoms in the molecule. At higher temperatures, chlorobenzene was also formed. Although in a low yield, 1,2,3-trichlorobenzene was found as a product of the reaction over Fe_3O_4 of 1,2,4-trichlorobenzene carried out at lower temperatures (Fig, 2(b)). Formation of the more crowded isomer is especially interesting. It can be a product of intramolecular rearrangement on which we have discussed previously with tribromobenzenes.11) However,

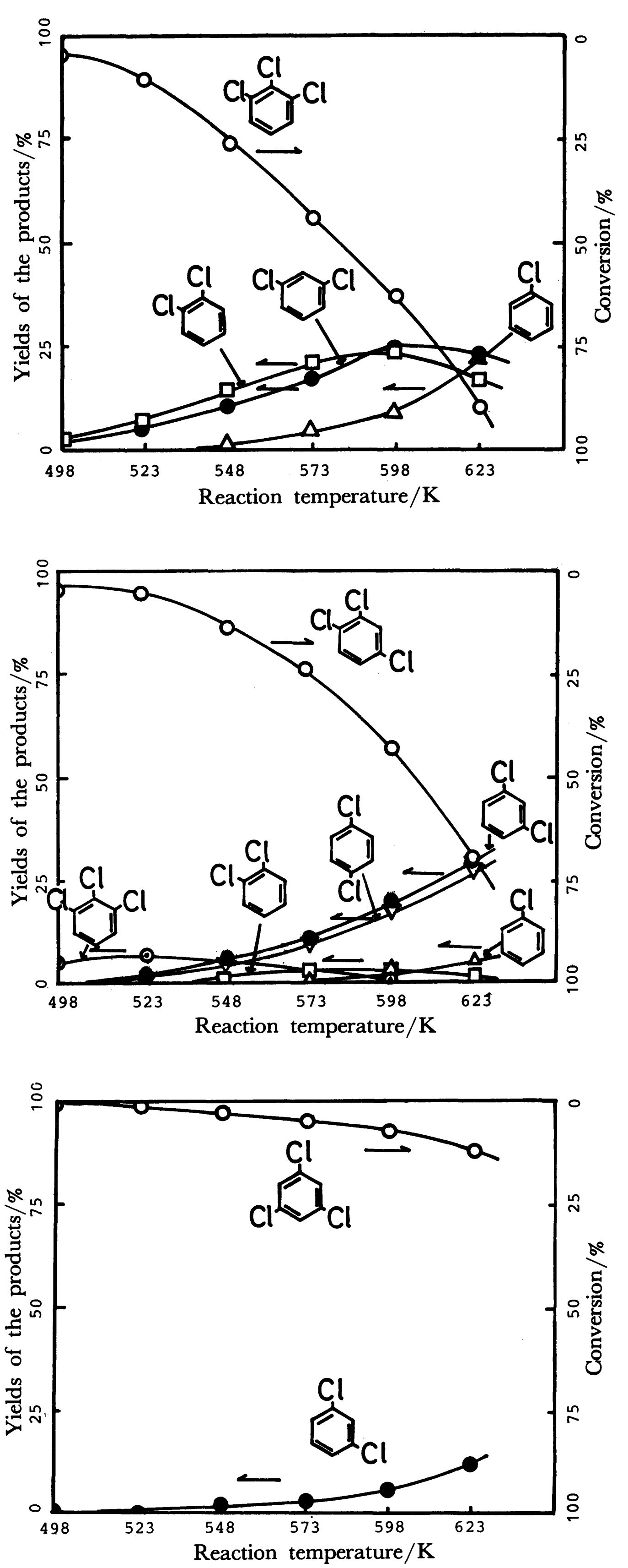

Fig. 2. Temperature dependence of the dechlorination products of isomeric trichlorobenzenes (on 550 mg of Fe_3O_4 pretreated with 500 μl of hexane). (a) 1,2,3-Trichlorobenzene, (b) 1,2,4-trichlorobenzene, and (c) 1,3,5-trichlorobenzene.

Table 2. Reactions of some neat chlorobenzenes over Fe_3O_4 at 623 K[a]

Substrate	Conversion	Produced (poly)chlorobenzenes/%									
	%	none	mono	ortho	meta	para	1,2,3	1,2,4	1,3,5	1,2,3,4	1,2,3,5&1,2,4,5
C_6H_5Cl	22.1	14.8	77.9	5.7	0.6	0.8	0.2				
o-$C_6H_4Cl_2$	27.6	19.5	0.4	72.4			6.5	1.2			
m-$C_6H_4Cl_2$	30.9	17.0	0.3	0.9	69.1		3.2	8.8	0.7		
$C_6H_3Cl_3$[b]	19.3	6.7	trace	0.1	0.4	0.4	5.0	80.7	trace	2.1	4.6
		(1)	(2)	(5)	(3)	(4)	(8)	(7)	(6)	(10)	(9)

a) 550 mg of Fe_3O_4 was used for the reaction. b) Numbers in paretheses correspond to the peaks in Fig. 3.

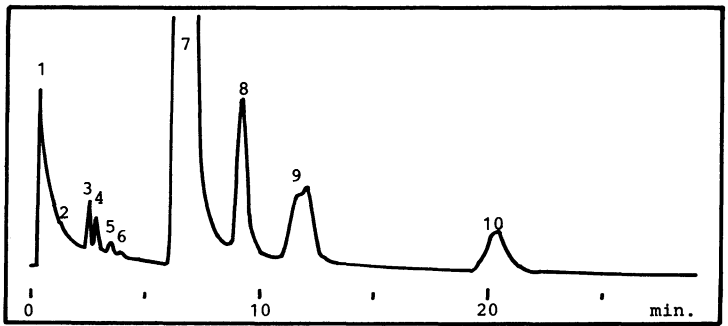

Fig. 3. Gas chromatogram of the products from neat 1,2,4-trichlorobenzene passed over Fe_3O_4 without pretreatment at 623 K. The numbers in this figure correspond to those of the products in Table 2.

further investigation is necessary to conclude the mechanism of its formation.

The dechlorination did not proceed when the benzene solution was injected, probably because benzene is a poor hydrogen donor in this reaction.

Dechlorination carried out by injecting neat polychorobenzene (chlorobenzene, o-dichlorobenzene, m-dichlorobenzene, and 1,2,4-trichlorobenzene) over pretreated Fe_3O_4 gave dechlorination products only in extremely low yields (Table 2). Alternatively, isomerized and highly substituted polychlorobenzenes were also detected as products. As an example, the gas chromatogram of the products from 1,2,4-trichlorobenzene is shown in Fig. 3. They might be formed secondarily by the substitution reactions by free chlorine atom (free radical) which is generated primarily by the cleavage of C–Cl bond, because the pattern of the substitution is rather random and suggestive of free radical reactions. The results resemble to those of the thermal decomposition of polybromobenzenes.[5]

In conclution, the following scheme can explain the overall reactions: (i) Hydrogen is supplied from hydrogen donor (solvent) prior to the dechlorination. (ii) Cleavage of C–Cl bond proceeds by the catalysis of Fe_3O_4 forming polychlorophenyl free radical. (iii) Generated free radical receives hydrogen very promptly from a hydrogen donor molecule or from the surface of partly hydrogenated Fe_3O_4. Another path alternative to (ii) and (iii) is also possible, in which (ii′) C–Cl bond is hydrogenolytically cleaved on the surface of the partly reduced Fe_3O_4 containing hydrogen. Chlorine atom formed in the second stage ((ii) or (ii′)) might be bound rather tightly on the surface. Formation of iron chloride is probable but not detected by any means (powder X-ray, surface IR, *etc.*). At present there is no decessive evidence to differentiate the two alternative mechanism.

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9) Repeated injection of the sample causes a gradual decrease in the dechlorination activity of Fe_3O_4. The activity tends to be constant after several (5 to 7) times of injection. Fe_3O_4 in this state still retains about 60% of initial activity. The decreased activity could be regained partly (60 to 70%) by injecting sufficient hexane as a hydrogen donor, some chlorinated hydrocarbons being released from the Fe_3O_4 powder during the process.

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