

Photochemical Dehalogenation of Polyhalobenzenes. I. Survey of the Reactivity in Hexane Solution¹⁾

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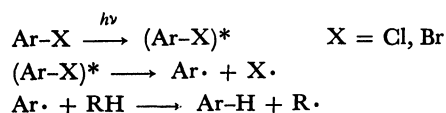
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Photochemical dechlorinations and debrominations of $C_6H_nX_{6-n}$ ($X=Cl, Br$) isomers were carried out in hexane. The products and residual reactant were determined quantitatively by means of gas chromatography. From these experiments, the relative rates of dehalogenation were obtained. The different rates among unequivalent sites in a molecule were interpreted by the effect of steric acceleration by the neighboring halogen atom(s). The reactivity of the halogen atom in polyhalobenzene towards photochemical elimination reaction is dependent both on its position in the molecule when compared among isomers and on the number of halogen atoms in a molecule when compared among polyhalobenzenes of various degrees of substitution. The latter effect is more predominant in the series of polybromobenzenes.

Physical properties of polyhalogenated aromatic compounds have been investigated rather extensively, since they were widely used as insulator, thermally stable heat-transfer medium and lubricant, and other purposes. On the other hand, reactions of these polyhaloaromatics were not known thoroughly because of their inertness towards most chemicals. Environmental contamination caused by polychlorinated biphenyls also attracted the attention to the chemical reactions of other polyhalogenated aromatics.²⁾ Considerably large number of investigations concerning their metabolism, toxicity, and abundance in environment were reported³⁾ together with the investigations on polychlorinated biphenyls. However, reactions of polyhalobenzenes have not been studied so extensively. In connection with the detoxication of polyhalogenated aromatic compounds, several photochemical dehalogenation procedures were reported in this decade.^{4,5)} Thus some polychlorinated biphenyls were successfully dechlorinated by irradiation of ultraviolet light in aqueous alkaline media.⁶⁾

Pinhey and Rigby,⁷⁾ and Ichimura and Mori⁸⁾ have studied the mechanism of dehalogenations of several rather simple haloarenes, showing that the photochemical process is the initial absorption of light causing $^1(\pi, \pi^*)$ excitation and subsequent intersystem crossing to $^3(\sigma, \sigma^*)$ state localized on a carbon-halogen bond, which induces the fission of the bond.



The abstraction of hydrogen from solvent (RH) is a thermal reaction of aryl free radical. Another explanation assuming the π -chlorobenzene intermediate, or transition state, was also proposed by Lemal⁹⁾ and have been contradicted by Arnold.¹⁰⁾

In our previous report,¹¹⁾ relative migrating ability of halogen atom of polyhalobenzenes in the Jacobsen type rearrangement was determined and the mechanism was discussed. In this connection, the photochemical dehalogenations were carried out on all possible polychloro- and polybromobenzene isomers, as well as

some polybromopolychlorobenzenes, in hexane in order to compare the reactivities of halogen (Cl or Br) atoms occupying different positions in a polyhalogenated benzene molecule. The products were analyzed quantitatively by gas chromatography, and the relative rate of dehalogenation of each dissimilar halogen atom was evaluated.

Experimental

Materials. Several tri-, tetra-, and pentabromobenzenes were prepared by the method previously reported by Furuyama *et al.*¹²⁾ Some of other polybromo-, polychloro-, and polybromopolychlorobenzenes were prepared by combination of direct halogenation and nitration followed by reduction and Sandmeyer reaction (replacement by halogen) of appropriately halogenated benzenes and anilines. Commercially available materials were used after purification by distillation or by chromatography. All of polyhalobenzenes were identified by their melting and/or boiling points and by spectral properties.

Reactions. Photo-reactions were carried out using a 30 W low pressure Hg lamp placed at the center of concentrically surrounded quartz vessel containing the solution of reactant. In some runs, a 100 W high pressure Hg lamp was also employed. The temperature of the solution was kept at 25 °C by external cooling, though the reaction is not dependent on the temperature of the solution. The solution was sampled at an interval of definite time (usually every two hours when the reaction is not very fast) and analyzed by gas chromatography.

Spectral and Chromatographic Measurements. GC/MS measurements were carried out on a Hitachi-6L or a Shimadzu LKB-9000B mass spectrometer. Routine gas chromatographic analyses of the products were carried out on a Shimadzu GC-6A apparatus or a GC-4B-PTF apparatus equipped with a polyethylene glycol 20M, a Silicone SE 30, or an Apiezon L column (3 mm × 2 m). UV/VS spectra and NMR spectra were recorded on a Shimadzu UV 365 and a JEOL FX 90Q spectrometers, respectively.

Results and Discussion

The photochemical reactions were pursued by quantitative GC analysis of the products and the starting

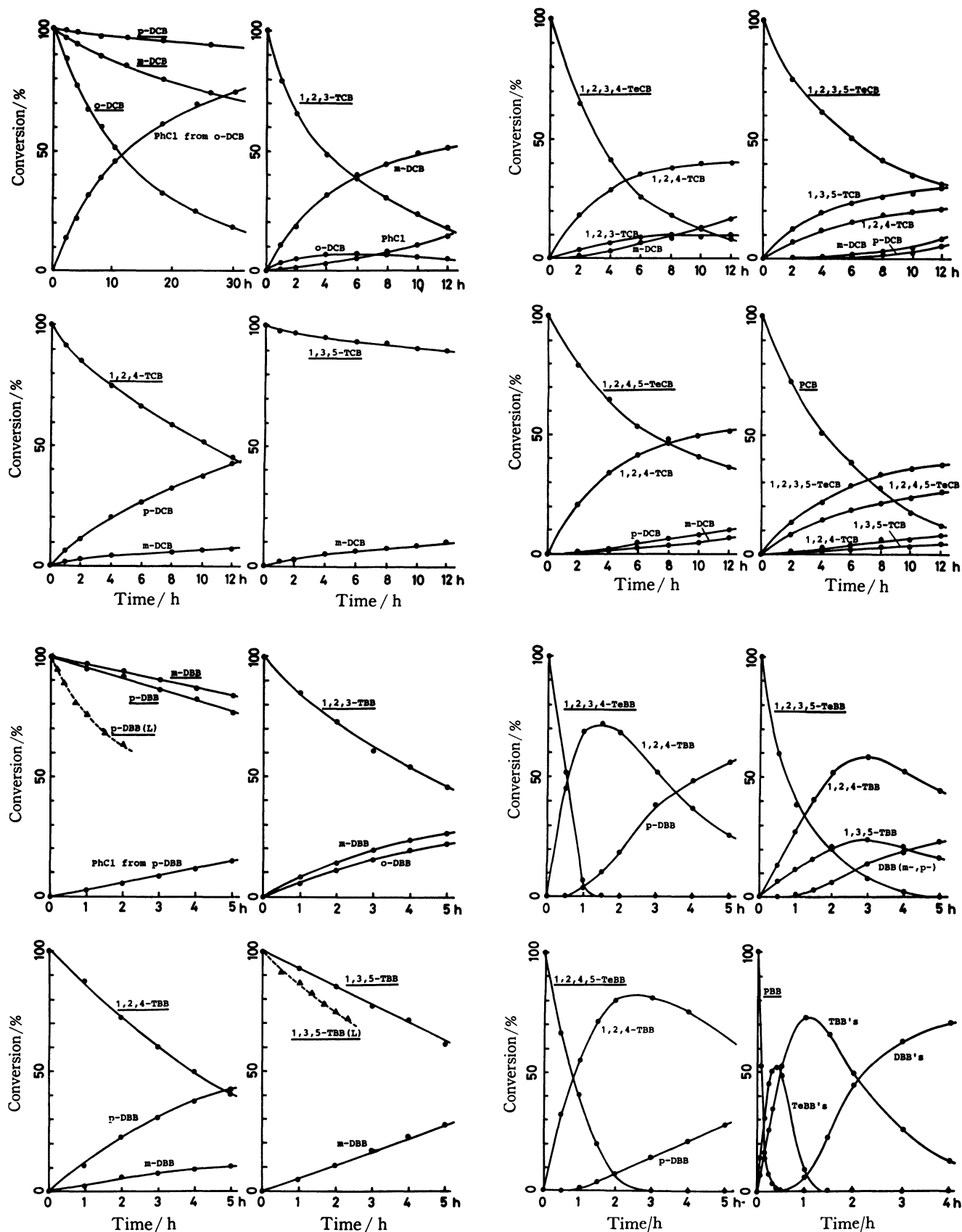


Fig. 1. Time-conversion curves for the photochemical dehalogenation of polyhalobenzenes. Experimental conditions are given in Table 1. In this figure, abbreviations such as following are used in order to name the starting materials and the products: *o*-DCB=*o*-dichlorobenzene, 1,2,3-TBB=1,2,3-tribromobenzene, 1,2,3,4-TeCB=1,2,3,4-tetrachlorobenzene, and so on. The starting material for each run is designated by underline in each diagram.

TABLE 1. RELATIVE RATES OF DEHALOGENATION (WITH REFERENCE TO THE MOST REACTIVE) IN HEXANE¹³⁾

a) Polychlorobenzenes (concn, 0.1 mol/l; temp, 25 °C; 30 W low pressure lamp)					c) Polybromopolychlorobenzenes (concn, 0.1 mol/l; temp, 25 °C; 30 W low pressure lamp)				
Substrate	No.	Position of leaving atom	Relative rate per site		No. of sites	Substituents on substrate	Conversion/ % ^{a)} after 4 h	Position of leaving atom	Relative rate within molecule
			Among isomers	Within molecule					
Dichlorobenzenes									
ortho	2a	—	1.00		2	1-Br-2, 3-Cl ₂	27.6	1-Br	1
meta	3a	—	0.21		2			2-Cl	0.04
para	4a	—	0.045		2			3-Cl	0.0
Trichlorobenzenes									
1,2,3	5a	1	0.13	(0.13)	2	1-Br-2, 4-Cl ₂	28.7	1-Br	1
		2	1.00	(1.00)	1			2-Cl	0.08
1,2,4	6a	1	0.15	(0.25)	1			4-Cl	0.0
		2	0.60	(1.00)	1	1-Br-3, 4-Cl ₂	30.0	1-Br	1
		4	0.03	(0.05)	1			3-Cl	0.24
1,3,5	7a	—	0.05		3			4-Cl	0.0
Tetrachlorobenzenes									
1,2,3,4	8a	1	0.15	(0.15)	2	1-Br-2, 3, 4-Cl ₃	18.3	1-Br	1
		2	1.00	(1.00)	2			2-Cl+3-Cl	0.09
1,2,3,5	9a	1	0.15	(0.33)	2			4-Cl	0.0
		2	0.46	(1.00)	1	1-Br-2, 3, 5-Cl ₃	28.9	1-Br	1
		5	0.0	(0.0)	1			2-Cl	0.08
1,2,4,5	10a	—	0.14		4			3-Cl, 5-Cl	0.0
Pentachlorobenzene									
1,2,3,4,5	11a	1		(0.0)	2	1-Br-2, 4, 6-Cl ₃	35.0	1-Br	1
		2		(0.81)	2			2-Cl, 4-Cl	0.0
		3		(1.00)	1	1-Br-2, 4, 5-Cl ₃	18.2	1-Br	1
b) Polybromobenzenes (concn, 0.05 mol/l; temp, 25 °C; 100 W high pressure lamp)									
Dibromobenzenes									
ortho	2b	—	0.87		2	1, 3-Br ₂ -4, 5-Cl ₂	25.0	1-Br	0.26
meta	3b	—	0.61		2			3-Br	1
para	4b	—	1.00		2			4-Cl, 5-Cl	0.0
Tribromobenzenes									
1,2,3	5b	1	0.25	(0.40)	2	1, 3-Br ₂ -2, 5-Cl ₂	18.2	1-Br	1
		2	0.62	(1.00)	1			2-Cl, 5-Cl	0.0
1,2,4	6b	1	0.26	(0.26)	1	1, 4-Br ₂ -2, 6-Cl ₂	35.0	1-Br	1
		2	1.00	(1.00)	1			4-Br	0.09
		4	0.0	(0.0)	1			2-Cl	0.0
1,3,5	7b	—	0.16		3	1, 2-Br ₂ -3, 5-Cl ₂	28.9	1-Br	0.43
Tetrabromobenzenes^{a)}									
1,2,3,4	8b	1	0.12	(0.12)	2			2-Br	1
		2	1.00	(1.00)	2			3-Cl, 5-Cl	0.0
1,2,3,5	9b	1	0.30	(0.73)	2	1, 2-Br ₂ -4, 5-Cl ₂	29.0	1-Br	1
		2	0.41	(1.00)	1			4-Cl	0.0
		5	0.0	(0.0)	1	1, 2, 3-Br ₃ -5-Cl	46.1	1-Br	0.34
1,2,4,5	10b	—	0.30		4			2-Br	1
Pentabromobenzene^{b)}									
1,2,3,4,5	11b	1		(0.0)	2			5-Cl	0.0
		2		(0.5)	2				
				(1.0)	1				

a) 0.0125 mol/l. b) 0.005 mol/l.

material. Since no quantitative consideration was taken on the intensity of the light for irradiation, only the relative reactivity will be discussed here. The time-conversion curves are given in Fig. 1.

In hexane solution, dehydrogenation reaction proceeds almost exclusively. In polyhaloarenes, elimination of halogen atom from different sites proceeds competitively as initial reactions from the excited state. The relative

rates of C-X (X=Cl, Br) bond fission, or the relative partial rate factors, are given in Table 1.

When the intramolecular reactivity of similar halogen atom is compared, the halogen atom flanked by two halogen atoms (at 2- and 6-positions) is the most reactive, and the one having an ortho halogen atom is the next most reactive. For example, the 2-halogen atom is the most reactive in the dehalogenations of all

a) The amounts of consumed starting polyhalobenzenes after 4 h are given, since the time-conversion curves are not shown in Fig. 1.

1,2,3-trihalogenated benzenes investigated (**5a**, **5b**, **8a**, **8b**, **9a**, and **9b**). This might be due to the steric and electrostatic repulsion caused by the neighboring halogen atoms. Elimination of halogen atom to give the corresponding aryl free radical reduces the steric hindrance of the molecule remarkably. Electronic effect caused by non-neighbor halogen atoms are rather complicated and cannot be related quantitatively to the electron densities and bond orders from molecular orbital calculations.¹⁴⁾ Empirically, the halogen substituent meta to the site of reaction accelerates the dehalogenation reaction more predominantly than the para substituent when other circumstances are similar. For example, the 2-halogen atom (having one ortho and one meta halogen) of 1,2,4-trihalobenzenes (**6a** and **6b**) are more reactive than the 1-halogen atom (having one ortho- and one para-halogen). When compared intermolecularly, the 2-halogen atom of 1,2,3,4-tetrahalobenzene (having two ortho and one meta halogen) are again more reactive than the 2-halogen atom of 1,2,3,5-tetrahalobenzene (having two ortho- and one para-halogen). The same is true also for the 1-bromine atom of 1-bromo-2,3,4-trichlorobenzene and 1-bromo-2,3,5-trichlorobenzene, and other cases investigated. Since the Hammett σ -constants for *m*-chloro (+0.373) and *m*-bromo (+0.391) substituents are more positive than the corresponding constants for para substituents (*p*-Cl, +0.226; *p*-Br, +0.232), implying that meta substituents are more electron-withdrawing than the para substituents, the destabilization can be expected by the second substitution by electronegative halogen atom. This can contribute to facilitate the release of the halogeno substituent even in the homolytic fission of carbon-halogen bond.

Differences in reactivity among the positional isomers are mainly determined by the positions of halogen atoms in the molecule. In general, 1,2,3-trihalobenzene reacts most promptly and 1,3,5-trihalobenzene most slowly among isomeric trihalobenzenes. Dehalogenation of 1,2,3,4-tetrahalobenzene is the fastest among the isomeric tetrahalobenzenes.

The effect of the number and the positions of halogen substitution is considerably different when compared quantitatively between the series of polychlorobenzenes and polybromobenzenes. In the series of polybromobenzenes, the reactivity tends to increase in the following order: monobromo < *o*-dibromo < *m*-dibromo < *p*-dibromo < 1,3,5-tribromo < 1,2,4-tribromo < 1,2,3-tribromo < 1,2,4,5-tetrabromo < 1,2,3,5-tetrabromo < 1,2,3,4-tetrabromo < pentabromo < hexabromo derivative. The rate of dehalogenation increases remarkably as the increase in the number of substituent halogen atoms even when statistic factor is taken into account (when the overall rate is divided by the number of halogen atoms on the benzene ring).¹⁵⁾ The photodehalogenation in this series of compounds were carried out using high pressure mercury arc (100 W). Two runs (with *p*-dibromo- and 1,3,5-tribromobenzenes) were carried out using low pressure mercury arc (30 W) which were used in the series of polychlorobenzenes. The overall patterns of time-conversion curves are very similar to each other.

In contrast to the reactions with polybromobenzenes, the reactivity of polychlorobenzene is very sensitive to the number of neighbor halogen atoms. As can be seen with *m*-dichloro-, *p*-dichloro-, and 1,3,5-trichlorobenzenes in Fig. 1, the rates of dechlorination of isolated chloro substituents (without ortho halogen substitution) are very low when compared with those carrying ortho halogen substituent(s). On the other hand, the rate of debromination is not so dependent on the neighboring halogen atoms. The total number of chloro-substituents on the benzene nucleus is less important than in the case of polybromobenzenes. Thus, the dehalogenations of 1,2,4-trichloro- and 1,3,5-trichlorobenzenes proceed approximately as fast as those of *o*-dichloro- and *m*-dichlorobenzenes, respectively. Increasing number of halogen substitution accelerates the reactions beyond the experimental error in polychlorobenzenes of higher degree of substitution, however.

As a consequence of the bond energy (C-Cl, 360 kJ/mol and C-Br, 297 kJ/mol) difference, the bond fission to produce the corresponding free radical proceeds more predominantly with C-Br bond than with C-Cl bond in the same molecule. Thus the debrominations take place almost exclusively in all dibromodichlorobenzenes investigated, giving corresponding bromodichlorobenzenes as primary products. No dibromochlorobenzenes were formed in detectable amounts in any runs, even if chlorobenzene (as a secondary product) was detected in some runs. In the reactions of several bromotrichlorobenzenes, dechlorination proceeds competitively with debromination. 1-Bromo-2,3,4-trichlorobenzene produces 1,2,3-trichloro- and 1-bromo-3,4-dichlorobenzenes in a 10 : 1 ratio after irradiation of 2 h. Similarly 1-bromo-2,3,5-trichlorobenzene gives 1,2,4-trichloro- and 1-bromo-3,5-dichlorobenzenes in a 12 : 1 ratio. In all cases debromination proceeds by far more promptly than dechlorination when both chloro and bromo substituents are located in the same molecule.

In order to confirm the difference in reactivity observed between polychloro- and polybromobenzenes more confidently, the photodehalogenations of some polyhalobenzenes were carried out in methanol. Methanol is another hydrogen-donating solvent from which the photochemically produced aryl free radical can abstract hydrogen atom, forming the dehalogenated product. Relative rates of dehalogenation in methanol are given in Table 2, reproducing the relative rates in hexane.

The effect of the nature of halogen (Cl or Br) on the

TABLE 2. RATES OF DEHALOGENATION OF DIHALOGENENES C_6H_4XY RELATIVE TO THE RATE OF *o*- C_6HCl_2 IN METHANOL (0.10 mol/l)

X	Y	<i>o</i> - C_6H_4XY	<i>m</i> - C_6H_4XY	<i>p</i> - C_6H_4XY	Product
Cl	Cl	1.00	0.25	0.04	C_6H_5Cl
Cl	Br	0.73 (1.00) ^{a)}	0.67 (0.91)	0.66 (0.89)	C_6H_5Cl
Br	Br	0.94 (1.00)	0.87 (0.92)	0.81 (0.86)	C_6H_5Br

a) Rates relative to the ortho-isomer of each series are given in parentheses.

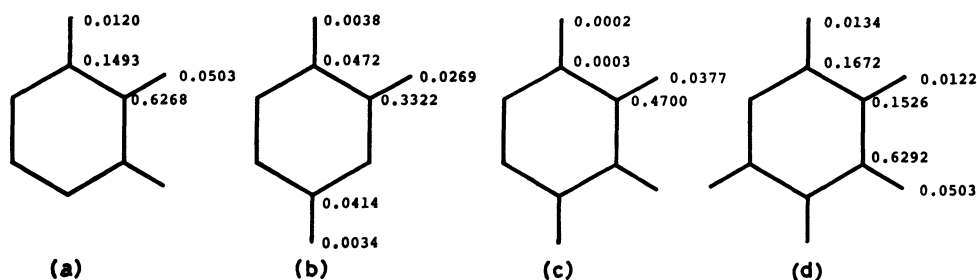


Fig. 2. π -LUMO densities of some polychlorobenzenes. (a) 1,2,3-Trichlorobenzene, (b) 1,2,4-trichlorobenzene, (c) 1,2,3,4-tetrachlorobenzene, and (d) pentachlorobenzene.

reactivity can be interpreted in the following way. In hexane, initial photolysis reaction of halobenzene to generate the corresponding aryl free radical might proceed similarly to the photolysis in gas phase. Thus the excited state leading to the photolytic cleavage of (carbon-halogen bond is expected to be the $^3(\sigma, \sigma^*)$ state localized on the breaking bond. Then the rates of dehalogenation should be determined by the probability of intersystem crossing from $^1(\pi, \pi^*)$ to $^3(\sigma, \sigma^*)$,⁸⁾ which is a function of both the energy difference of these two states and the LUMO(π^*) density on the breaking bond¹⁴⁾ if the wavelength and the intensity of incident light is invariable. The halogen substituent(s) ortho to the reaction site might weaken the carbon-halogen bond and lower the $^3(\sigma, \sigma^*)$ state due to the steric and electrostatic repulsive interaction. Since the energy difference between the $^1(\pi, \pi^*)$ and the $^3(\sigma, \sigma^*)$ states is supposed to be small in the case of chlorinated benzenes, the neighboring halogen effect lowering the $^3(\sigma, \sigma^*)$ state may favor the release of chlorine atom drastically under certain conditions sufficing the energetic requirement for the conversions involved. In contrast, the energy of the $^3(\sigma, \sigma^*)$ state localized on the breaking C-Br bond is considerably lower than the $^1(\pi, \pi^*)$ state in participation, and the assistance by the repulsive force does not affect their reactivities seriously. Effect of the number of substituent halogen atoms is far more predominant in the series of polybromobenzenes. This cannot be attributed to the simple steric effect due to the buttressing by the second neighbor halogen atoms. In this case, participation of direct $^3(\sigma, \sigma^*)$ or $^3(n, \sigma^*)$ excitation by irradiation is suspected owing to the contribution of heavy atom effect by bromine.¹⁶⁾

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- 13) During the preparation of our manuscript, dehalogenation of isomeric tetrachlorobenzenes in 2-propanol was reported (M. Usui, T. Nishiwaki, K. Anda, and M. Hida, *Nippon Kagaku Kaishi*, **1982**, 638). Their results are in line with those in this Table.
- 14) The densities of LUMO(π^*) by simple LCAO-MO calculation could be correlated with the reactivity of polychlorobenzenes (and polybromobenzenes), however. Except the case of 1,2,3,5-tetrachlorobenzene whose LUMO has a node along the most reactive C-Cl bond because of its symmetrical property, all trichloro-, tetrachloro-, and pentachlorobenzenes have the largest LUMO density on the most reactive C-Cl bond (that is to say, the largest LUMO density of all carbon atoms and the largest LUMO density among chlorine atoms in the molecule) as given in Fig. 2. The large LUMO density will favor the intersystem crossing on the $^1(\pi, \pi^*)$ state to the $^3(\sigma, \sigma^*)$ state localized on the respective C-Cl bond.
- 15) Our experiment shows that the rates of conversion were related very close to the inverse of concentration, showing that the rate is controlled by the intensity of irradiated light. Substantial retarding effect by the increase of concentration was observed towards the end of reaction, which might be due to the deposit of solid or resinous secondary products on the surface of reaction vessel and also due to the coloration of the reaction mixture.
- 16) Possibility of the participation of direct S-T absorption has been pointed out by Soumillon and the co-worker in the photo-dechlorination of 2,4-dichloroanisole (J. Ph. Soumillon and J. Vermeulen, *Bull. Soc. Chim. Belg.*, **91**, 474 (1982)). Thus the participation of direct S-T excitation is very probable in the photo-reactions of polybromo aromatic compounds.