Photochemistry of π-Complexes of Chlorine Atom with Methyl- and Ethyl-Substituted Benzenes

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The photochemistry of π-complexes of the chlorine atom with a series of methyl- and ethyl-substituted benzenes has been investigated using combined pulse radiolysis-laser flash photolysis techniques. Direct photolysis of π-complexes in carbon tetrachloride causes photobleaching by intramolecular hydrogen abstraction with quantum yields of 0.05-0.15 depending on the substituents but not on the positions of them.

In the previous studies on the photochemistry of π-complexes between diphenyl sulfide and chlorine atoms, photobleaching due to the intermolecular hydrogen abstraction was observed.[1] In the case of π-complexes between mesitylene and chlorine atoms in carbon tetrachloride and 1,2-dichloroethane, on the other hand, the solvent independent intramolecular hydrogen abstraction has been reported to occur with a quantum yield of 0.10.[2] Since the increased selectivity of the tertiary hydrogen abstraction in photochlorination of alkanes was attributed to the formation of π-complexes of chlorine atoms with benzene,[3] the kinetic studies of the arene/chlorine atom π-complexes have been extensively carried out by many workers.[4-6] In the course of the kinetic studies of the selectivty of hydrogen abstraction based on the partial reactivity,[7] we have found the significant effects of methyl substituents on the reaction rate constants of the ground state arene/chlorine atom π-complexes with various alcohols as shown in Table 1.[8] The reaction rate constants decrease by almost one order as the number of the methyl-substituents increases. The purpose of this study is to obtain further experimental bases of the substituent effects to understand the photochemistry of π-complexes.

The π-complexes of chlorine atoms with various methyl- and ethyl-substituted benzenes were produced on irradiation of deaerated carbon tetrachloride solutions of 2×10^{-2} mol dm^{-3} substituted benzenes with a 30 ns width, 45 MeV electron pulse. Figure 1 shows transient absorption spectra of ethylbenzene and 1,3-diethylbenzene observed immediately after the pulse. The UV-Vis absorption bands can be easily characterized as those due to the π-complexes on the basis of assignment made for benzene and methylated benzenes in the previous studies.[9-12]

Figure 2 shows kinetic traces obtained by pulse radiolysis and pulse radiolysis-laser flash photolysis[13] of 1,2,4-trimethylbenzene in carbon tetrachloride. Laser flash photolysis (6 ns width pulses of 337 nm from N_2-laser) caused rapid and permanent photobleaching. Actinometry was performed with solutions of benzophenone (1.0×10^{-3} mol dm^{-3}) containing naphthalene (1.0×10^{-1} mol dm^{-3}), and the extinction coefficients of π-complexes were estimated assuming the radiation chemical yield of the chlorine atom in carbon tetrachloride to be 0.17 μmol J^{-1} as described previously.[2] The quantum yields of photobleaching obtained are listed in Tables 2 and 3 for methyl- and ethyl-substituted benzenes, respectively. This photobleaching can be attributable to the intramolecular hydrogen abstraction as suggested in the previous study on mesitylene/Cl π-complexes.[2] The quantum yield increases as the number of methyl-substituents increases, from 0.05 for toluene to 0.15 for hexamethylbenzene (Table 2). This tendency is in a marked contrast to those observed for the intermolecular hydrogen abstraction of ground state π-complexes from alcohols (Table 1). It should be noted that the

Table 1. Reaction rate constants of the π-complexes between chlorine atom and arene toward alcohols

	k(arene/Cl + ROH) / 10^7 dm^3 mol^{-1} s^{-1}			
	benzene	toluene	m-xylene	mesitylene
ethanol	25	0.58	0.13	0.073
1-butanol	33	5.4	0.16	0.029
1-pentanol	40	6.2	1.3	0.27

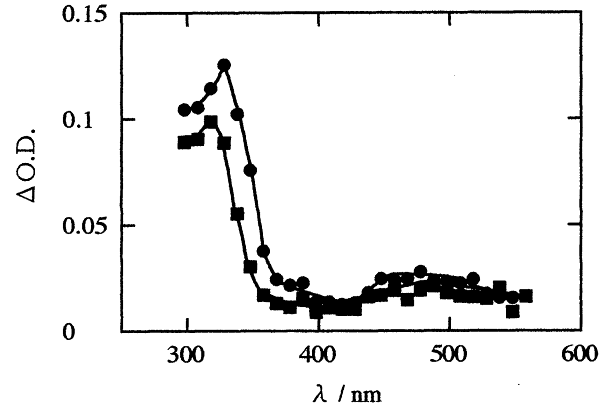

Figure 1. Transient absorption spectra of π-complexes obtained immediately after pulse radiolysis of ethylbenzene (■) and1,3-diethylbenzene (●) in carbon tetrachloride.

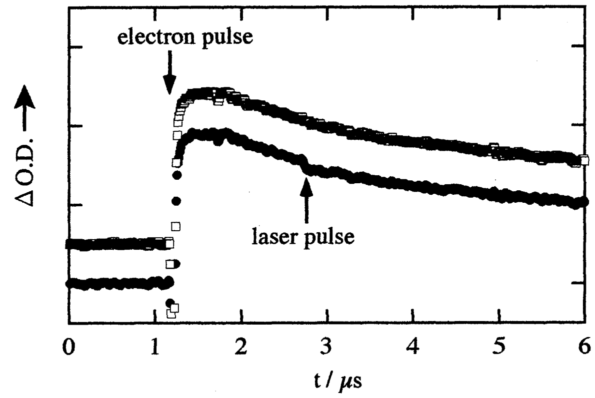

Figure 2. Pulse radiolysis (□) and pulse radiolysis-laser flash photolysis (●) of 2×10^{-2} mol dm^{-3} 1,2,4-trimethylbenzene in CCl_4 observed at 318 nm.

Table 2. Quantun yields of photobleaching of π-complexes of chlorine atom with methyl-substituted benzenes in CCl_4

Arene	Quantum Yield
PhMe	0.05 ± 0.02
1,2-$Me_2C_6H_4$	0.08
1,3-$Me_2C_6H_4$	0.10
1,4-$Me_2C_6H_4$	0.10
1,2,3-$Me_3C_6H_3$	0.09
1,2,4-$Me_3C_6H_3$	0.11
1,3,5-$Me_3C_6H_3$	0.12
1,2,3,4-$Me_4C_6H_2$	0.14
1,2,3,5-$Me_4C_6H_2$	0.13
1,2,4,5-$Me_4C_6H_2$	0.13
Me_5C_6H	0.15
Me_6C_6	0.15

Table 3. Quantun yields of photobleaching of π-complexes of chlorine atom with ethyl-substituted benzenes in CCl_4

Arene	Quantum Yield
PhEt	0.13 ± 0.02
1,2-$Et_2C_6H_4$	0.14
1,3-$Et_2C_6H_4$	0.13
1,4-$Et_2C_6H_4$	0.13

position of the methyl groups gives no effects on the quantum yields, *i.e.* , almost the same quantum yields within the experimental error were obtained among isomers.

As can be seen from Table 3, ethyl-substituted benzenes give much higher quantum yields than corresponding methyl-substituted ones. These tendencies can be well explained by the bond dissociation energy[14] of the related atoms: 464.0 ($H-C_6H_5$), 431.62 (H-Cl), 368.2 ($H-CH_2C_6H_5$), 357.3 kJ mol^{-1} ($H-CH(CH_3)C_6H_5$). From these values it is clear that ethyl groups are more easy to hydrogen release by chlorine atoms. Therefore, the increase of the intramolecular hydrogen abstraction quantum yields with increasing the number of methyl groups should be due to statistical effects. On the other hand, the effects of methyl groups on the reaction rate constants of ground state π-complexes with alcohols (Table 1) may be explained by the increase of basicity with increasing the number of methyl groups.[15] The increase of basicity of arenes should contribute to the stabilization of the π-complexes between chlorine atoms and arenes which leads to the decreasing reactivity of the π-complexes toward alcohols.

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