Quantum Yields of Intramolecular Hydrogen Abstraction Induced by Laser Flash Photolysis of Arene/Cl π-Complexes

Feng Wu, Toshihiko Shindo, Sadashi Sawamura, and Takashi Sumiyoshi*

Division of Quantum Energy Engineering, Graduate School of Engineering, Hokkaido University,
Kita-13, Nishi-8, Kita-ku, Sapporo 060

(Received April 7, 1997)

Arene/chlorine atom π-complexes were generated by pulse radiolysis of a wide variety of substituted benzenes in carbon tetrachloride at room temperature. Upon laser flash photolysis of the π-complexes, intramolecular hydrogen abstraction was observed in times much shorter than the flash time (6 ns), with quantum yields between 0.05 and 0.18 depending on the sort and the number of the substituents but not on their positions. The effects of substituents on the photochemistry of arene/chlorine atom π-complexes were discussed in connection with the bond dissociation energy of the related atoms and with the structure of the π-complexes.

About 40 years ago, Russell suggested that the increased selectivity for abstraction of hydrogen attached to the tertiary carbon atom in photochlorination of alkanes would be attributed to the formation of π-complexes of chlorine atoms with benzene.[1,2] After that, the kinetic studies of the arene/Cl π-complexes have been carried out extensively by many workers.[3—9] The application of the idea of the partial reactivity[10] to hydrogen abstraction of free chlorine atoms[11] and benzene/Cl π-complexes[12] from various alcohols has clearly shown the higher tertiary/primary selectivity of π-complexes. Recently, we reported that methyl-substituents exhibit a significant effect on the rate constants for reactions of ground state arene/Cl π-complexes with various alcohols.[13] It was found that the reaction rate constants decrease by almost one order as the number of methyl-substituents increases by one. This change can be explained by the increase of basicity with increasing the number of methyl groups.[14] The increase of basicity of arenes contributes to the stabilization of the π-complexes with chlorine atoms and leads to the decreasing reactivity of the π-complexes toward alcohols.

Recently, the photochemistry of π-complexes of halogen atoms with diphenyl sulfide and mesitylene has been investigated using combined pulse radiolysis-laser flash photolysis techniques.[15] Permanent photobleaching was observed, depending on both solvents and counter halogen atoms. While no photochemistry was observed for Br complexes with either molecule, permanent photobleaching was induced by intermolecular hydrogen abstraction of excited diphenyl sulfide/Cl π-complexes from solvents ($\Phi = 0.05$ in 1,2-dichloroethane). On the other hand, in the case of mesitylene/Cl π-complexes, permanent photobleaching resulted from intramolecular hydrogen abstraction with no dependence on solvents ($\Phi = 0.10$). In this work, we have investigated the effects of the kind, the number and positions of substituents on the reaction process of various arene/Cl π-complexes in excited states, using combined pulse radiolysis-laser flash photolysis techniques. A series of methyl-substituted benzenes and their isomers (from toluene to hexamethylbenzene), several ethyl-substituted benzenes (from ethylbenzene to 1,3,5-triethylbenzene), and other alkyl-substituted benzenes were studied. In addition, benzene derivatives with methoxy groups and with methoxy and methyl groups were also investigated.

Experimental

Materials. All samples of methyl- and ethyl-substituted benzenes (special guaranteed reagent grade) except 1,3,5-triethylbenzene from Tokyo Kasei were used as received. The other alkyl-substituted benzenes, methoxy-substituted benzenes, benzene, carbon tetrachloride (spectral grade), naphthalene (scintillation grade), and benzophenone (special guaranteed reagent grade) from Wako were also used as received.

Irradiation. The conventional pulse radiolysis setup with a time resolution of 10 ns was used to produce arene/Cl π-complexes. Electron pulses of 45 MeV and 30 ns in duration from an S-band linear accelerator were used as an irradiation source. The dose per pulse in the present study was 130—200 Gy measured by the KSCN dosimeter. For the flash photolysis studies of arene/Cl π-complexes, the irradiations were carried out at 337.1 nm with an N_2-laser (Usho, YKN-900). The flash duration was 6 ns. Actinometry was performed with solutions of benzophenone (1.0×10^{-3} mol dm^{-3}) containing naphthalene (1.0×10^{-1} mol dm^{-3}). The optical absorption of the naphthalene triplets formed by energy transfer from the benzophenone triplets was measured ($\varepsilon_{425\,\mathrm{nm}} = 1.32\times10^4$ dm^3 mol^{-1} cm^{-1},[16] $\Phi = 1.0$[17]). The maximum laser output per pulse was 2.5 mJ.

Solutions containing 2×10^{-2} mol dm^{-3} substituted benzenes were deaerated with a stream of argon and sealed with a Teflon® valve. The electron and laser beam were collinearly focused to a 6 mm diameter spot. To observe transient optical absorption signals, the analyzing light from a 1 kW xenon arc lamp was passed through the sample perpendicularly to both electron and laser pulses. All experiments were carried out at room temperature (15±2 °C).

Results and Discussion

Transient Absorption Spectra of Various Substituted Benzene/Cl π-Complexes. Figure 1 shows transient absorption spectra of 1,3,5-triethylbenzene (a) and 1,3-dimethoxybenzene (b) in carbon tetrachloride observed immediately after an electron pulse. There are two absorption bands around 340 and 500 nm in both spectra. These UV-vis absorption bands can be easily characterized as arene/Cl π-complexes on the basis of assignments made for benzene/Cl and methylated benzene/Cl π-complexes in the previous studies.[18—20] For the other substituted benzenes, the spectra similar to those shown in Fig. 1 were also obtained. Considering the position of the band around 340 nm and the shape of the spectra of various arene/Cl π-complexes, these π-complexes can be excited by a laser pulse of 337.1 nm.

Photobleaching of Various Arene/Cl π-Complexes. Figure 2a shows a kinetic trace observed at 328 nm on pulse radiolysis of 1,3,5-triethylbenzene in carbon tetrachloride which illustrates formation and decay of 1,3,5-triethylbenzene/Cl π-complexes. The change of the transient optical absorption of the π-complexes induced by laser flash photolysis at 1.2 μs after the electron pulse is shown in Fig. 2b. It is seen that π-complexes are bleached during a laser pulse (6 ns) and decay without recovering. The difference of the optical density due to photobleaching (Figs. 2a and 2b) is given in Fig. 2c. These results indicate that a part of π-complexes were photobleached permanently on photolysis.

Figure 3 shows kinetic traces of 1,3-dimethoxybenzene observed at 328 nm in carbon tetrachloride by pulse radiolysis (a), pulse radiolysis-laser flash photolysis (b), and subtraction of b from a (c), respectively. In the case of methoxy-substituted benzenes, the decay rates of π-complexes were higher than those of alkyl-substituted ones, which would bring difficulties in observation of small change of transient optical absorptions; however, photobleaching was evidenced by the subtraction result shown in Fig. 3c.

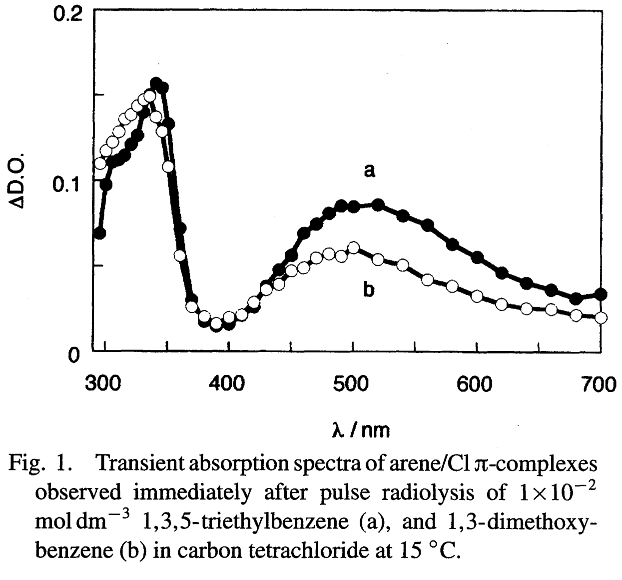


Fig. 1. Transient absorption spectra of arene/Cl π-complexes observed immediately after pulse radiolysis of 1×10^{-2} mol dm^{-3} 1,3,5-triethylbenzene (a), and 1,3-dimethoxybenzene (b) in carbon tetrachloride at 15 °C.

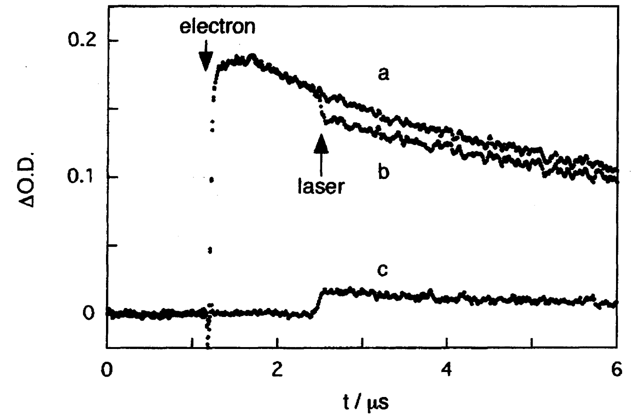


Fig. 2. Absorbance changes at 328 nm vs. time of 1×10^{-2} mol dm^{-3} 1,3,5-triethylbenzene in carbon tetrachloride observed by pulse radiolysis (a), and combined pulse radiolysis-laser flash photolysis (b), and changes of absorbance due to photobleaching of π-complexes (c) obtained by subtraction of b from a.

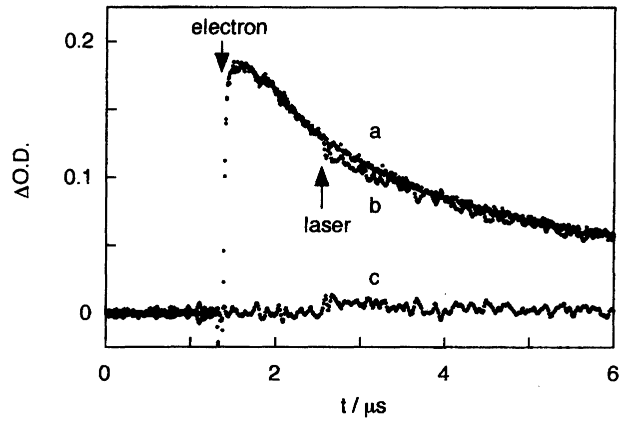


Fig. 3. Absorbance changes at 328 nm vs. time of 1×10^{-2} mol dm^{-3} 1,3-dimethoxybenzene in carbon tetrachloride observed by pulse radiolysis (a), and combined pulse radiolysis-laser flash photolysis (b), and changes of absorbance due to photobleaching of π-complexes (c) obtained by subtraction of b from a.

The effects of solvents (carbon tetrachloride and 1,2-dichloroethane) and concentration of arenes on the quantum yields of permanent photobleaching were investigated. It is shown that the photobleaching is not dependent on solvents or on concentration of arene. This result agrees with those reported in the previous studies on mesitylene/Cl π-complexes,[15] i.e., these photobleachings can be attributed to intramolecular hydrogen abstraction of arene/Cl π-complexes.

Furthermore, in order to elucidate whether the intramolecular hydrogen abstraction of arene/Cl π-complexes occurs on a benzene ring or on the substituents, nonsubstituted benzene/Cl π-complexes were investigated. According to the kinetic traces obtained by pulse radiolysis-laser flash photolysis of benzene/Cl π-complexes, photobleaching was not observed with our experimental system (the limit of detection:

ΔO.D.$_{\text{bleach}} > 0.003$). On the other hand, photobleaching as shown in Figs. 2b and 3b was observed for all substituted benzene/Cl π-complexes. Therefore, we conclude that the hydrogen atom involved in intramolecular hydrogen abstraction comes from the substituents rather than from a benzene ring.

In the previous study,[15)] we reported a mechanism of the intramolecular hydrogen abstraction induced by excitation of mesitylene/Cl π-complexes as follows (Scheme 1).

According to the present experimental results, we assume that the mechanism of intramolecular hydrogen abstraction for substituted benzenes/Cl π-complexes except for benzene is the same as that depicted in Scheme 1.

Quantum Yields of Photobleaching. The quantum yields of photobleaching by intramolecular hydrogen abstraction of various substituted benzene/Cl π-complexes were determined using the difference kinetic traces obtained by subtracting the kinetic traces obtained by pulse radiolysis-laser flash photolysis from those obtained by pulse radiolysis. The extinction coefficients of π-complexes were estimated assuming the radiation chemical yield of the chlorine atom in neat carbon tetrachloride to be 0.17 μmol J^{-1} as described previously.[15)] The quantum yields of photobleaching thus obtained for methyl-, ethyl-, alkyl-, and methoxy-substituted benzenes are listed in Tables 1, 2, 3, and 4, respectively.

Table 1. Quantum Yields of Photobleaching of Methyl-Substituted Benzene/Cl π-Complexes in CCl_4

Arene	Φ_{bleach}
$C_6H_5CH_3$	0.05 ± 0.02
1,2-$C_6H_4(CH_3)_2$	0.08
1,3-$C_6H_4(CH_3)_2$	0.10
1,4-$C_6H_4(CH_3)_2$	0.10
1,2,3-$C_6H_3(CH_3)_3$	0.11
1,2,4-$C_6H_3(CH_3)_3$	0.11
1,3,5-$C_6H_3(CH_3)_3$	0.12
1,2,3,4-$C_6H_2(CH_3)_4$	0.14
1,2,3,5-$C_6H_2(CH_3)_4$	0.13
1,2,4,5-$C_6H_2(CH_3)_4$	0.13
$C_6H(CH_3)_5$	0.15
$C_6(CH_3)_6$	0.15

Table 2. Quantum Yields of Photobleaching of Ethyl-Substituted Benzene/Cl π-Complexes in CCl_4

Arene	Φ_{bleach}
$C_6H_5C_2H_5$	0.13 ± 0.02
1,2-$C_6H_4(C_2H_5)_2$	0.14
1,3-$C_6H_4(C_2H_5)_2$	0.13
1,4-$C_6H_4(C_2H_5)_2$	0.13
1,3,5-$C_6H_3(C_2H_5)_3$	0.18

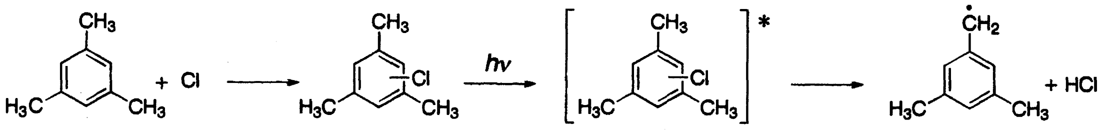
Table 3. Quantum Yields of Photobleaching of Alkyl-Substituted Benzene/Cl π-Complexes in CCl_4

Arene	Φ_{bleach}
$C_6H_5CH_3$	0.05 ± 0.02
$C_6H_5C_2H_5$	0.13
$C_6H_5C_3H_7$	0.11
$C_6H_5C_4H_9$	0.12
$C_6H_5C_5H_{11}$	0.12
$C_6H_5CH(CH_3)_2$	0.14

Table 4. Quantum Yields of Photobleaching of Methoxy-Substituted Benzene/Cl π-Complexes in CCl_4

Arene	Φ_{bleach}
$C_6H_5OCH_3$	0.04 ± 0.02
1,2-$C_6H_4(OCH_3)_2$	0.05
1,3-$C_6H_4(OCH_3)_2$	0.05
1,2-$C_6H_4(OCH_3)CH_3$	0.08
1,3-$C_6H_4(OCH_3)CH_3$	0.08
1,4-$C_6H_4(OCH_3)CH_3$	0.10

Tables 1 and 2 indicate the influence of the number and the position of substituents on quantum yields. As can be seen from Table 1, the quantum yields of methyl-substituted benzenes increase from 0.05 to 0.15 as the number of methyl-substituents increases. But in the case of ethyl-substituted benzenes there is no clear increase of quantum yields with increasing substituents from ethylbenzene to diethylbenzenes. It should be noticed from the data in Tables 1 and 2 that the same quantum yields were obtained among isomers within the experimental errors. From these data, it is clear that the quantum yields of photobleaching of arene/Cl π-complexes are not affected by the position of substituents. These results can be well explained by consideration of the structures for arene/Cl π-complexes. In the previous theoretical and experimental studies, arene/Cl π-complexes were supposed to possess C_{6v} symmetry,[7,20)] and the structure of the arene/Cl π-complexes was speculated to have a chlorine atom positioned directly above the center of the benzene ring. Jarzeba et al.[21)] suggested, however, that the chlorine atom of benzene/Cl π-complexes was positioned slightly outside of the benzene ring at 101° to the plane of the ring by ab initio calculations. If arene/Cl π-complexes had the structure which they suggested, the quantum yields of photobleaching of substituted benzene/Cl π-complexes should be different among isomers, i.e., the quantum yields should be affected by the position of substituents. However, in the present experimental results, such an effect can not be observed. Therefore, it is concluded that the structure of benzene/Cl π-complexes agrees with the suggested one, in which a chlorine atom is positioned directly above the center of the benzene ring. It



Scheme 1.

should be noted that the above calculations were carried out for the structure of π-complexes in the gas phase.

As can be seen from Table 3, among monoalkyl-substituted benzenes, toluene has the smallest quantum yield of photobleaching (0.05), while for ethyl-, propyl-, butyl-, and pentylbenzene, almost the same quantum yields (0.11—0.13) were obtained within the experimental errors. According to the results above, it is apparent that the length of normal chains of alkyl-substituents beyond an ethyl group exhibits no effect on the quantum yield of photobleaching. Besides, for cumene with a branched chain, almost the same quantum yield as that of ethylbenzene was also obtained. If hydrogen atoms in the outer methyl groups of cumene were concerned in photobleaching, the quantum yields should be twice that of ethylbenzene. Therefore, it can be deduced that the hydrogen atom involved in the intramolecular hydrogen abstraction comes from the substituents in which the hydrogen atoms are bonded to carbon atoms directly connected to a benzene ring. Considering the results for toluene ($\Phi = 0.05$) and ethylbenzene (0.13), the smaller bond dissociation energy of cumene hydrogen compensates for the difference of the number of hydrogen atoms which can be abstracted (vide infra).

The photobleaching quantum yields for methoxy-substituted benzenes are smaller than those of corresponding methyl-substituted ones (Table 4). In the case of methoxy- and methyl-substituted benzenes, similar quantum yields to those of dimethylbenzenes were obtained. It is also observed here again that the positions of substituents, whether the substituents are the same kind or not, have no effect on the quantum yields.

The absence of photobleaching in the case of benzene and certain trends in the dependence of quantum yields of photobleaching due to intramolecular hydrogen abstraction on the substituents can be recognized with the aid of the bond dissociation energy of the related atoms. The bond dissociation energy[22] of the hydrogen atoms are : 464.0 (H-C_6H_5), 431.62 (H-Cl), 368.2 (H-$CH_2C_6H_5$), 357.3 (H-CH-$(CH_3)C_6H_5$), 353.1 kJ mol^{-1} (H-$C(CH_3)_2C_6H_5$). From these values, we can expect larger quantum yields for ethyl-substituted benzenes than those for methyl-substituted ones. The increase of quantum yields for the methyl-substituted benzene/Cl π-complexes with increasing the number of methyl groups should be due to statistical effects. Since hydrogen abstraction from benzene by chlorine atoms is an endothermic reaction the photobleaching of excited benzene/Cl π-complexes is not an efficient process. Even though the bond dissociation energy of anisole has not been reported, the reason why the quantum yield for anisole is lower than that of toluene can be deduced from the difference of the distance between Cl and H on the substituents. It is notable that this explanation is based on the structure of C_{6v} symmetry of π-complexes discussed above.

The authors are very grateful to Messrs Hiroaki Tanida and Koichi Sato for their help in operating the linac.

References

1) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 2977 (1957).

2) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

3) C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

4) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

5) P. S. Skell, H. N. Baxter, III, and C. K. Taylor, *J. Am. Chem. Soc.*, **105**, 120 (1983).

6) P. S. Skell, H. N. Baxter, III, J. M. Tanko, and V. Chebolu, *J. Am. Chem. Soc.*, **107**, 5464 (1985).

7) K. D. Raner, J. Lusztyk, and K. U. Ingold, *J. Am. Chem. Soc.*, **111**, 3652 (1989).

8) K. U. Ingold, J. Lusztyk, and K. D. Raner, *Acc. Chem. Res.*, **23**, 219 (1990).

9) S. Förgeteg and T. Bérces, *J. Photochem. Photobiol. A: Chem.*, **73**, 187 (1993).

10) M. Anbar, D. Meyerstein, and P. Neta, *J. Chem. Soc. B*, **1966**, 742.

11) T. Sumiyoshi and M. Katayama, *Trends Phys. Chem.*, **1**, 7 (1992).

12) T. Sumiyoshi, *Radiat. Phys. Chem.*, in press.

13) F. Wu, T. Sumiyoshi, Y. Yamashita, T. Shindo, and S. Sawamura, *Chem. Lett.*, **1996**, 643.

14) E. C. Brown and D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

15) a) T. Sumiyoshi, H. Sakai, M. Kawasaki, and M. Katayama, *Chem. Lett.*, **1992**, 617; b) T. Sumiyoshi, M. Kawasaki, and M. Katayama, *Bull. Chem. Soc. Jpn.*, **66**, 2510 (1993).

16) R. Bensasson and E. J. Land, *Trans. Faraday Soc.*, **67**, 1904 (1971).

17) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

18) R. E. Bühler and M. Ebert, *Nature* (*London*), **214**, 1220 (1967).

19) R. E. Bühler, *Chim. Acta*, **51**, 1558 (1968).

20) K. D. Raner, J. Lusztyk, and K. U. Ingold, *J. Phys. Chem.*, **93**, 564 (1989).

21) W. Jarzeba, K. Thakur, A. Hörmann, and P. F. Barbara, *J. Chem. Phys.*, **99**, 2016 (1995).

22) "CRC Handbook of Chemistry and Physics," 76th ed, ed by D. R. Lide, CRC Press, Boka Raton (1995).