Charge-Transfer Spectra of Halogen Atoms and the Halogenation Reaction of Aromatics Studied by the Flash Technique

Naoto Yamamoto, Takao Kajikawa, Hiroyasu Sato, and Hiroshi Tsubomura

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan. *Received July 5, 1968*

Abstract: Flash photolysis of molecular bromine as well as iodine was studied in benzene and toluene at room temperature. Transient absorption spectra were observed which are attributable to the charge-transfer complexes formed between the halogen atoms and the aromatics. Flash photolysis of bromine in deoxygenated toluene initiates the bromination chain reaction followed by complete disappearance of bromine molecules. It is of interest that a transient absorption, probably due to a charge-transfer-type interaction, appears even for such a reactive system.

Numerous papers on the halogenation reaction of organic substances have been reported.[1] It has been confirmed from kinetic studies that the halogenation occurs by the radical chain mechanism initiated by halogen atoms which are produced photochemically or by other methods in gas phase[2,3] or in liquid phase.[4-6] From the selectivity on the position of attack of chlorine atoms upon hydrocarbons, Russell concluded that, in various aromatic solvents, halogen atoms form complexes with the aromatics.[6]

More recently, Rand and Strong have observed transient absorption bands by the flash photolysis of iodine in benzene or other aromatic solvents and attributed them to the charge-transfer complexes of atomic iodine with the aromatics.[7,8] The similar experiment was also carried out by Gover and Porter,[9] who arrived at the same conclusion.

Experimental Section

Iodine was purified twice by sublimation. EP grade bromine was used without further purification. Thiophene-free benzene was purified by dissolving a small amount of iodine in it and illuminating for 10 hr with a 250-W high-pressure mercury lamp. Iodine was then removed by extraction with 0.02 *M* sodium sulfate solution. The benzene was allowed to stand for a day with potassium carbonate and distilled over sodium. Toluene was shaken with concentrated sulfuric acid, washed, neutralized by addition of sodium hydroxide, and then washed with water. Thiophene-free toluene produced was allowed to stand for a day with potassium carbonate, dried with sodium, and distilled.

Sample solutions were poured into a quartz reaction cell 1.5 cm in diameter and 20 cm in optical path length, and deoxygenated with a stream of purified nitrogen gas for 1 hr. Because the solutions containing both bromine and toluene were photochemically reactive, they were prepared in the dark as described below. A cell having a side arm connected to two ampoules was used. The solutions, several times as much as the volume sufficient to fill up the cell, were deoxygenated by bubbling nitrogen gas in one of the ampoules covered with black paper. The cell was filled with the solution by transferring it from the ampoule just before every flash irradiation. After the flash irradiation, the photolyzed solution was transferred from the cell into the other ampoule.

The flash photolysis apparatus was the same as described elsewhere.[10] The durations of the photolysis flash and the spectroflash were 4 μsec or less. The photolysis flash was in most cases fired with the total electric energy of 160 J.

Results and Discussion

Firstly, we reexamined the flash photolysis of iodine in some aromatic solvents at room temperature. The solutions were photolyzed with the flash light through a filter transparent in the wavelength region longer than 450 mμ. The transient absorption spectrum obtained after flash photolysis of a 3.2×10^{-5} *M* solution of iodine in benzene had an absorption maximum at 465 mμ (Figure 1a). The intensity of the band declined to one-half of the initially observed value at 50 μsec after the flash. Similarly, for a 1.9×10^{-5} *M* toluene solution, a transient absorption was obtained. The spectra obtained are nearly in agreement with those by Strong *et al.*,[8] and hence we tentatively assign the spectra to the charge-transfer bands of the complexes formed between atomic iodine and the solvents. The iodine atoms produced are presumed to recombine rapidly, and the final concentration of iodine after each of the flash experiments stayed almost the same as that of the original one.

Flash photolysis of a deoxygenated solution of about 10^{-2} *M* bromine in benzene resulted in a transient absorption as shown in Figure 1b, with a maximum at 555 mμ. The electron affinity of bromine atom is considerably larger than that of iodine atom.[11] It may, therefore, be expected that, for a given donor molecule, a complex of bromine atom as an acceptor has a charge-transfer band in the longer wavelength region than in the case of iodine atom. If the assignment for the case of iodine is true, it is reasonable that the transient absorption obtained here is assigned to the charge-transfer band of a complex formed between the bromine atom and benzene.

---

[1] For example, see C. Walling, "Free Radicals in Solution," John Wiley Sons, Inc., New York, N. Y., 1957, Chapter 8; D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Co., New York, N. Y., 1967, Chapter 10.

[2] E. W. Swegler, H. A. Scheraga, and E. R. VanArtsdalen, *J. Chem. Phys.*, **19**, 135 (1951).

[3] H. R. Anderson, Jr., H. A. Scheraga, and E. R. VanArtsdalen, *ibid.*, **21**, 1258 (1953).

[4] R. E. Pearson and J. C. Martin, *J. Am. Chem. Soc.*, **85**, 354 (1963).

[5] K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958).

[6] G. A. Russell, *ibid.*, **79**, 2977 (1957); **80**, 4987, 4997, 5002 (1958).

[7] S. J. Rand and R. L. Strong, *ibid.*, **82**, 5 (1960).

[8] R. L. Strong, S. J. Rand, and J. A. Britt, *ibid.*, **82**, 5053 (1960).

[9] T. A. Gover and G. Porter, *Proc. Roy. Soc.* (London), **A262**, 476 (1961).

[10] N. Yamamoto, Y. Nakato, and H. Tsubomura, *Bull. Chem. Soc. Japan*, **39**, 2603 (1966).

[11] R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38**, 1540 (1963).

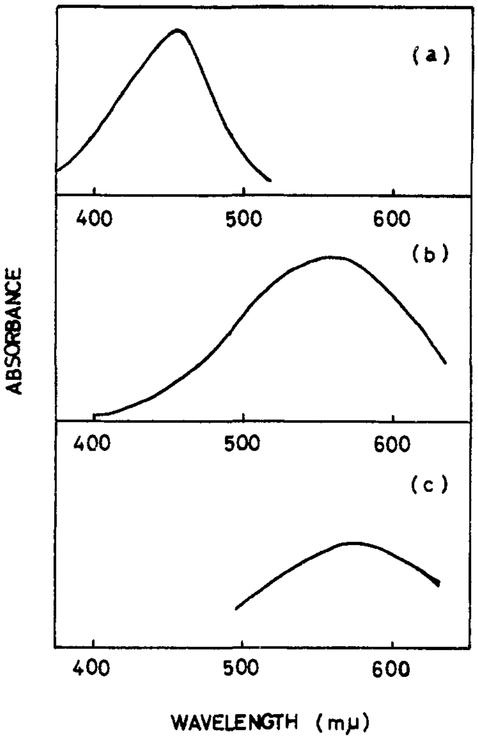

Figure 1. Transient absorption spectra which appeared by a flash photolysis of (a) 3 × 10^{-5} *M* iodine in benzene, (b) about 10^{-2} *M* bromine in benzene, and (c) 6 × 10^{-3} *M* bromine in toluene. The spectra are obtained by subtracting the absorption spectrum of the solution before flash photolysis from that after photolysis.

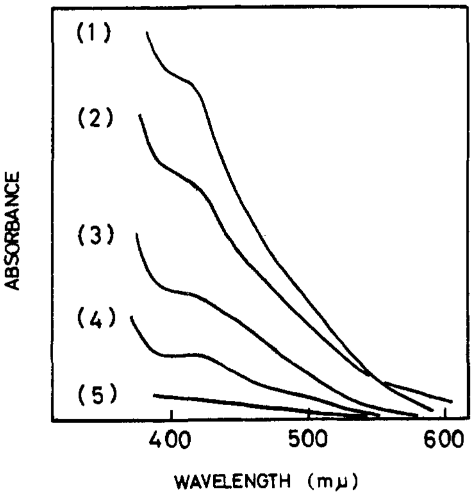

Figure 2. Decay of the absorption spectra of molecular bromine caused by the flash photolysis of 8 × 10^{-3} *M* bromine in toluene: (1) before the flash, (2) at 5 μsec, (3) at 28 μsec, (4) at 56 μsec, (5) at 460 μsec.

The flash photolysis of a 6 × 10^{-3} *M* solution of bromine in toluene gave a transient absorption spectrum centered at 575 mμ as shown in Figure 1c, where the solution was photolyzed with the flash light through a soda glass filter which is transparent in the wavelength region longer than 310 mμ. The absorption almost disappeared in less than 20 μsec. The maximum of the absorption band lies at a slightly longer wavelength than that ascribed to the charge-transfer complex of benzene. The energy difference between them is in fairly good accord with the difference between the charge-transfer bands of atomic iodine with benzene and toluene. Thus the absorption may as well be ascribed to a charge-transfer complex of bromine atom with toluene. After the flash irradiation, the concentration of the molecular bromine dissolved in the solution kept on diminishing, until all the bromine disappeared with one single flash.

Recently, Bühler and Ebert found a transient absorption spectrum attributed to a charge-transfer complex of chlorine atom with benzene at 490 mμ by the radiolysis of carbon tetrachloride solution of benzene.[12] Our results combined with that obtained by Bühler and Ebert show that the energies of charge-transfer excitation of the benzene complexes with various halogen atoms decreases in the order I, Cl, Br. This does not agree with the order which might be expected from the electron affinities of the halogen atoms: I < Br < Cl.[11] However, this discrepancy might not be a fatal objection against our interpretation of the transient absorption band, because there are many other factors influencing the wavelengths of the charge-transfer bands. For instance, the splitting between the ground configurations and the charge-transfer configurations may be larger for the case of chlorine than for the case of bromine because of the presumably stronger interaction in the former case. Similar discrepancy from the linear relationship between the wave numbers of the charge-transfer complexes and the ionization potentials of donor molecules is well known for some strong complexes such as iodine–amines.

Recently, Strong has also studied the photoproduction and recombination of bromine atoms by flash photolysis of molecular bromine in carbon tetrachloride, which did not serve as a donor. He did not observe any absorption bands assigned to the charge-transfer complex.[13]

It is well known that irradiation of a solution containing both molecular halogen and some organic substances results in the halogenation of the latter with a very large quantum yield. Goldfinger proposed the mechanism of the halogenation reaction of toluene with N-chlorosuccinimide.[14] By applying the mechanism to the case of photochemical reaction of bromine in liquid toluene (RH), the following reaction scheme may be expected as the main process

$$\mathrm{Br_2} + h\nu \longrightarrow 2\mathrm{Br} \qquad (1)$$

$$\mathrm{Br} + \mathrm{RH} \longrightarrow \mathrm{Br}\cdots\mathrm{RH} \qquad (2)$$

$$\mathrm{Br}\cdots\mathrm{RH} \longrightarrow \mathrm{R}\cdot + \mathrm{HBr} \qquad (3)$$

$$\mathrm{R}\cdot + \mathrm{Br_2} \longrightarrow \mathrm{RBr} + \mathrm{Br} \qquad (4)$$

where R· denotes benzyl radical and Br···RH a charge-transfer complex of bromine atom with toluene.

For the purpose of studying the halogenation reaction processes in detail by the flash technique, the decay of the concentration of molecular bromine was followed as a function of time after the flash. An 8 × 10^{-3} *M* solution of bromine in deoxygenated and dried toluene was flash-photolyzed at room temperature. The electric energy of the photolysis flash was 90 J, and a filter transparent in the wavelength region longer than 450 mμ was used. The result is shown in Figure 2. A strong ab-

---

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

(13) R. L. Strong, *J. Am. Chem. Soc.*, **87**, 3563 (1965).

(14) J. Adam, P. A. Grosselain, and P. Goldfinger, *Nature*, **171**, 704 (1953).

sorption in the wavelength region shorter than 400 mμ is due to the charge-transfer band of the complex between molecular bromine and toluene,[15] and a shoulder at 405 mμ is due to the characteristic absorption band of molecular bromine. Within 10 μsec after the flash, there is a slight increase of absorption in the region 570–650 mμ, and the decrease of the concentration of molecular bromine was rather slight. Then, most of the disappearance of bromine takes place in the dark period. About one-half of molecular bromine disappeared at 15 μsec after the flash. This fact confirms that almost all the bromine disappeared by the secondary processes initiated by the flash excitation. Until now, the halogenation reaction mechanism has been studied only by the kinetic analysis. Our result is an example directly showing that the halogenation is based on the chain reaction such as shown above.

We have also found that such a chain reaction did not occur when aerated solutions were used, indicating that the benzyl radical as an intermediate in the chain reaction reacts with oxygen dissolved in the solutions.[16]

We have also studied the flash photolysis of a solution of bromine in benzene in the presence of 10^{-2} *M* toluene. Even in this system, an absorption band similar to that of the charge-transfer complex between atomic bromine and benzene appeared at about 10 μsec after the flash irradiation. All of the bromine molecules disappeared with a single flash irradiation. The rate of the decrease of concentration of molecular bromine was nearly equal to that obtained in liquid toluene. If the mechanism described above for the chain reaction is true, this result suggests that reaction 4, which is diffusion controlled, should be the rate-determining step. Benzyl radical formed has a strong absorption in the near-ultraviolet region, but its absorption in the visible region is very weak.[17] In the present experiment, the measurement in the ultraviolet region was very difficult, owing to the strong absorption of the halogen and the reaction products. The concentration of the benzyl radical during the chain reaction must be very low, and it is reasonable that we did not find any absorption due to the benzyl radical in the visible region.

---

(15) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, 72, 4677 (1950).

(16) According to the result by Strong, the amount of iodine atom formed in various organic solvents was not affected by the presence of oxygen (see ref 8).

(17) G. Porter and B. Ward, *J. Chim. Phys.*, 1517 (1964).

Electrogenerated Chemiluminescence. III. Intensity–Time and Concentration–Intensity Relationships and the Lifetime of Radical Cations of Aromatic Hydrocarbons in N,N-Dimethylformamide Solution

Stephen A. Cruser and Allen J. Bard[1]

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received June 5, 1968*

Abstract: The intensity–time behavior observed during electrogenerated chemiluminescence (ECL) for multiple cycles and for cases where one of the radical ions is unstable has been investigated. Working curves, obtained by digital computer simulation, are presented which allow determination of the rate constants for the decomposition of the radical ions. The half-lifes of the cation radicals of 9,10-diphenylanthracene, 1,3,6,8-tetraphenylpyrene, and rubrene were determined experimentally. The maximum ECL intensity, obtained by passing alternating current through the cell, was, in all cases, a linear function of the concentration of the electroactive species.

Most of the previous reports of electrogenerated chemiluminescence (ECL) have dealt with proposed mechanisms and with observation of the phenomenon itself.[2] Little attention has been paid to quantitative treatments of the problems of mass transfer and kinetics during ECL, particularly upon repeated cycling. Feldberg[3] has derived, using digital computer techniques, theoretical equations relating, quantitatively, the light intensity produced in ECL to the current, time, and kinetic parameters using a double potential step mode of generation and assuming the light-producing reaction is an anion-radical–cation-radical annihilation followed by radiative decay. Experimental verification of Feldberg's equations has been reported for the ECL of rubrene, under conditions where both ion radicals are stable for the duration of the experiment.[4,5]

We report here an extension of Feldberg's digital simulation technique to allow for additional reactions of the ion radicals and for multiple cycles. In this case, the theoretical intensity–time curves are indicative of the stability of the radicals involved in the annihilation reaction. Several aromatic hydrocarbons have been investigated and the half-lives of the radical cations

---

(1) To whom correspondence and requests for reprints should be directed.

(2) T. Kuwana, "Electroanalytical Chemistry," Vol. I, A. J. Bard, Ed., Marcel Dekker, Inc., New York, N. Y., 1966, Chapter 3, and references contained therein.

(3) (a) S. W. Feldberg, *J. Am. Chem. Soc.*, 88, 390 (1966); (b) *J. Phys. Chem.*, 70, 3928 (1966).

(4) J. Chang, D. M. Hercules, and D. K. Roe, *Electrochim. Acta*, 13, 1197 (1968).

(5) R. E. Visco, and E. A. Chandross, *ibid.*, 13, 1187 (1968).