

# Photochemistry of halogenated anilines studied by time-variation of microwave dielectric absorption

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## Abstract

The photochemistry of *p*-halogenated anilines ( $\text{H}_2\text{NC}_6\text{H}_4\text{X}-p$  (XA)) such as *p*-chloroaniline (CA; X = Cl), *p*-bromoaniline (BA; X = Br), and *p*-iodoaniline (IA; X = I) in benzene has been studied by the time-variation of microwave dielectric absorption (MWDA) method with respect to the transient behavior of the excited states and intermediates with independent dipole moments. The formation and the transient behavior of CA in the triplet excited state ( $^3\text{CA}^*$ ) having the ion pair character of [*p*-aminophenyl cation/ $\text{Cl}^-$ ], an ion pair of [*p*-aminophenyl cation/ $\text{Br}^-$ ], and a *p*-aminophenyl radical were observed in benzene from the time profiles of the MWDA signals immediately after the laser flash during 308-nm laser irradiation of CA, BA, and IA. The yields of the cleavage of the C–X bond were in the order of CA < BA < IA which reflects the order of the bond dissociation energy (BDE), CA > BA > IA. Decay of  $^3\text{CA}^*$  having the character of [*p*-aminophenyl cation/ $\text{Cl}^-$ ] was observed with a lifetime of 3.8  $\mu\text{s}$ . The homolytic cleavage of the C–Br bond in  $^3\text{BA}^*$  occurs to give a radical pair [*p*-aminophenyl radical/Br] which sequentially gives an ion pair [*p*-aminophenyl cation/ $\text{Br}^-$ ] through electron transfer between radicals. The dissociation of the [*p*-aminophenyl cation/ $\text{Br}^-$ ] to the *p*-aminophenyl cation and  $\text{Br}^-$  was observed to occur on a 20  $\mu\text{s}$  time scale. On the other hand, homolytic cleavage of the C–I bond in  $^3\text{IA}^*$  occurs efficiently to give the *p*-aminophenyl radical and I. Bimolecular reactions of  $^3\text{CA}^*$  having the character of the [*p*-aminophenyl cation/ $\text{Cl}^-$ ] with oxygen and a *p*-aminophenyl radical with oxygen were found to occur at rate constants of  $8.3 \times 10^7$  and  $10^8$ – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

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## 1. Introduction

It has been established based on the product analysis and transient absorption measurements that heterolytic cleavage of the C–X bond of halogenated anilines ( $\text{H}_2\text{NC}_6\text{H}_4\text{X}$ ; X = Cl, Br, I) occurs mainly in polar solvents to give the aminophenyl cation and a halide ion ( $\text{X}^-$ ) in their photochemistry [1,2]. The aminophenyl cation is stabilized by equilibration with triplet 4-iminocyclohexa-2,5-dienylidene. In contrast, the homolytic cleavage of the C–X bond of halogenated benzenes ( $\text{C}_6\text{H}_5\text{X}$ ) has been recently shown to occur to give the phenyl radical and halogen atom (X) [3]. Electron transfer between the phenyl radical and X is followed to yield a phenyl cation and  $\text{X}^-$  as the intermediates [4,5]. Photoionization of  $\text{C}_6\text{H}_5\text{X}$  (X = Br, I) giving the radical cation occurs together with homolytic cleavage of the C–X

bond giving the phenyl cation and X, and the cleavage of the C–X bond of the radical cation occurs to give the phenyl cation and X [3]. Aniline in the excited triplet state is generated and deactivated to the ground state without product formation in the photochemistry of aniline [4,5].

Although the photochemistry of halogenated anilines, halogenated arenes, and anilines has been studied mainly in polar solvents by product analysis and laser flash photolysis, the reaction mechanisms involving excited states and intermediates are unclear because the lack of clear absorption of such chemical species. From the time-resolved absorption measurements in polar solvents, it is difficult to distinguish between free ions and radical ion pairs and between free radicals and radical pairs. Because chemical species should have chromophores with large absorption coefficients to be detected with the absorption measurements, most of the intermediates are composed of aromatic groups. In contrast to the photochemistry of halogenated anilines, halogenated arenes, and anilines in polar solvents, the photochemical reactions occur in a significantly small yield in a non-polar solvent because of fast recombination of the radical ion

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pairs generated initially. No transient absorption measurement has been reported during the laser flash photolysis in non-polar solvents.

In the present study, we have studied the photochemistry of *p*-halogenated anilines ( $\text{H}_2\text{NC}_6\text{H}_4\text{X-}p$  (XA); X = Cl, Br, I) in benzene with the time-variation of microwave dielectric absorption (MWDA) measurement. This MWDA method does not depend on characteristic chromophores to monitor transient species and therefore can be used to study the transient behavior of the dipole moment of molecules in non-polar solvents. Molecular structure and reactivity based on the dipole moment of molecules have been studied usually by various spectroscopic methods and molecular-orbital calculations. However, these methods are not suitable for investigating the transient behavior of molecules in the excited states and short-lived species. On the other hand, the transient measurement on a microsecond time scale is possible in the MWDA method in which the time-variation of the MWDA signal can be measured based on the dielectric relaxation of a polar molecule in non-polar solvents [6,7]. Dipole moments of molecules in the excited states and short-lived species can be determined by the MWDA method. Moreover, the transient phenomena of species, unimolecular, and bimolecular reaction rates and lifetimes, can be studied. In addition, the MWDA method can be applied to study chemical reactions involving radicals, ions, radical pairs, ion pairs, or CT-complexes with the independent dipole moments.

Formation and reaction of ion pairs in non-polar solvents cannot be studied by laser flash photolysis of XA because of the lack of transient absorption to monitor. In contrast, the photochemistry of amine/halogenated compounds as electron-donor/acceptor molecules has been studied in non-polar solvents by the MWDA method. Shimamori et al. have reported the formation of a contact ion pair of aniline and carbon tetrachloride in the photochemistry in non-polar solvents [7]. Here we report the photochemistry of XA such as *p*-chloroaniline (CA), *p*-bromoaniline (BA), and *p*-iodoaniline (IA) in benzene as a non-polar solvent by the MWDA method. Because XA has donor and acceptor sites in the molecule, a large change in the dipole moment in the excited state or intramolecular electron transfer may be involved in the photochemistry.

## 2. Experimental section

The sample was irradiated with a 308-nm laser pulse from an excimer laser (Lambda Physik, LPX 205i). An X-band microwave circuit was used. A silica cell containing the sample solution was placed within the resonant cavity ( $\text{TE}_{101}$  mode, resonant frequency 8.8 GHz, loaded  $Q > 3000$ ). During irradiation of the laser pulse, the MWDA signal was detected by a crystal diode. The signal was amplified and transmitted to a Tektronix 2430 digital oscilloscope. The response time of the apparatus was about 150 ns. The signal was mostly taken with one shot of the laser pulse. The

laser intensity was 3.0 mJ per pulse for most measurements. The MWDA signal is produced only when photolysis causes changes in the dipole moment of the solute or in the polarity due to production of transients as a result of the photochemical reactions, and no component from the solvent is involved except that the signal sensitivity is associated with the dielectric constant of the solvent. When a transient species is generated having a dipole moment larger than that of the starting molecule during photoirradiation, we can observe an increase in the signal amplitude. When the dipole moment of a transient species is smaller than that of the starting molecule, decreases in the signal amplitude can be observed.

Photolysis of diphenylcyclopropanone (DPCP (dipole moment, 5.1 D)) was used as the reference. Photodissociation of this compound gives nonpolar products (diphenylacetylene (0 D) and CO (0.1 D)) [6]. As described above, the quantum yield of this reaction is approximately 1.0 for irradiation at 308 nm, because the yield is 1.0 for irradiation at 337 nm.

CA, BA, IA, (Tokyo Kasei) and DPCP (Aldrich) were purified by fractional sublimation. Benzene (Wako, spectral grade) as the solvent was used without purification. The samples were prepared in a transparent rectangular cell made of quartz (0.2 cm  $\times$  1.0 cm  $\times$  4.0 cm, optical-path length of 0.2 cm) at room temperature and were saturated with Ar or oxygen for 15 min. The concentration of sample solutions was chosen to have an absorbance of 1.0 at 308 nm of the excitation laser wavelength. Concentrations of CA, BA, and IA in benzene were  $2.6 \times 10^{-3}$ ,  $2.9 \times 10^{-3}$ , and  $3.1 \times 10^{-3}$  M, respectively.

## 3. Results and discussion

### 3.1. Photochemistry of CA in benzene

The time-variation of microwave dielectric absorption was observed during 308-nm laser flash photolysis of CA in Ar-saturated benzene (Fig. 1a). The MWDA signal with an amplitude of 25 was obtained immediately after the flash and decayed with a lifetime of 3.8  $\mu\text{s}$  according to the first-order rate equation. The MWDA signals with an amplitude of 25 and 18 in air- and oxygen-saturated benzene, respectively, were observed to be similar to 25 in Ar-saturated benzene (Table 1), while the decay was

Table 1  
Amplitude of the microwave dielectric absorption signal observed during laser photolysis of  $\text{H}_2\text{NC}_6\text{H}_4\text{X}$  (X = Cl, Br, I) in Ar-, Air-, and oxygen-saturated benzene

Aniline	Ar-saturated	Air-saturated	O <sub>2</sub> -saturated
CA	25	25	18
BA	93	120	145
IA	-25	48	78

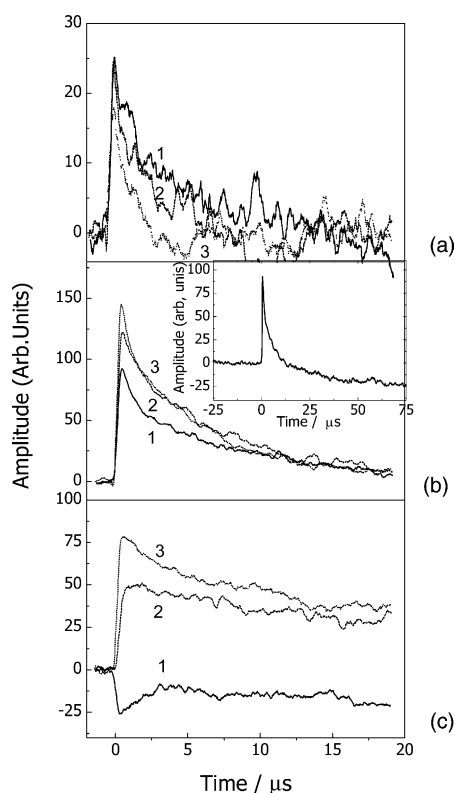
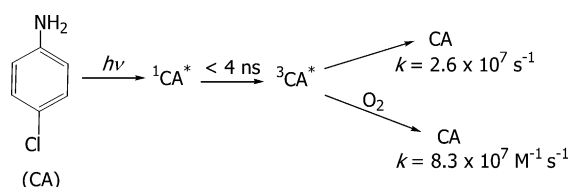


Fig. 1. Time-variation of microwave dielectric absorption observed during 308-nm laser flash photolysis of (a) CA, (b) BA, and (c) IA in Ar-saturated (solid line, 1), air-saturated (broken line, 2), and oxygen-saturated (dashed line, 3) benzene at room temperature. The inset in (b) shows the signal observed in the time scale of 75  $\mu\text{s}$  in Ar-saturated benzene.

accelerated in oxygen-saturated benzene compared with that in Ar-saturated benzene (Fig. 1a). The signal was quenched by oxygen with a bimolecular rate constant of  $8.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  calculated from the observed rate constant and the concentration of saturated oxygen in benzene ( $9.02 \times 10^{-3} \text{ M}$ ).

Guizzard et al. [1] and Othmen et al. [2] have reported that CA in the triplet excited state ( $^3\text{CA}^*$ ) with a weak absorption peak at 450 nm is initially generated and decomposes to a *p*-aminophenyl cation with a weak absorption peak at 430 nm and chloride ion ( $\text{Cl}^-$ ) through heterolytic cleavage of the C–Cl bond mainly in polar solvents during the laser flash photolysis. However, the transient behavior of  $^3\text{CA}^*$  is not clear because of overlapping of the absorption with the *p*-aminophenyl cation and further intermediates. The formation quantum yields of the *p*-aminophenyl cation and  $\text{Cl}^-$  depended on the solvents in the range of 0.03 in benzene and 0.5 in polar solvents based on product analysis. On the other hand, Shimamori and Sato have found that the lifetime of  $^3\text{aniline}^*$  is 1.2  $\mu\text{s}$  in benzene from the MWDA measurement [8]. The dipole moment ( $\mu$ ) of CA has been reported to be 2.35 D [9], while the  $\mu$  of  $^3\text{CA}^*$  is 4.26 and 3.06 based on the spectroscopic measurement [10] and the MWDA method [8,11,12], respectively. Because the  $\mu$  of the contact ion pair of  $\text{aniline}^+/\text{CCl}_4^-$  has been reported to



Scheme 1.

be 9 D [7], a large  $\mu$  value is expected for the contact ion pair of [*p*-aminophenyl cation/ $\text{Cl}^-$ ].

Based on our results together with the data reported, it is suggested that the MWDA signal generated immediately after the laser flash is assigned to  $^3\text{CA}^*$  having the ion pair character of [*p*-aminophenyl cation/ $\text{Cl}^-$ ]. The decay with a lifetime of 3.8  $\mu\text{s}$  corresponds mainly to deactivation of  $^3\text{CA}^*$  to CA in the ground state, because the heterolytic cleavage of the C–Cl bond giving the contact ion pair of *p*-aminophenyl cation and  $\text{Cl}^-$  with a large dipole moment occurs in a low yield [5]. The bimolecular rate constant of  $8.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  for the reaction of  $^3\text{CA}^*$  and oxygen in benzene is smaller than  $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for a related aromatic compound in the triplet state [2]. The one-order magnitude slower rate constant is explained by the character of  $^3\text{CA}^*$  having the ion pair character of [*p*-aminophenyl cation/ $\text{Cl}^-$ ].

This is the first report on the detection, decay, and reaction with oxygen for  $^3\text{CA}^*$  having the ion pair character of [*p*-aminophenyl cation/ $\text{Cl}^-$ ] (Scheme 1).

### 3.2. Photochemistry of BA and IA in benzene

The MWDA signal with an amplitude of 93 in Ar-saturated benzene was observed during 308-nm laser flash photolysis of BA in Ar-saturated benzene (Fig. 1b). The amplitude was three times larger than 25 in the case of CA (Table 1). On the other hand, a signal with an amplitude of  $-25$  was observed during 308-nm laser flash photolysis of IA in Ar-saturated benzene (Fig. 1c). Therefore, the MWDA signals show the formation of transient species with larger and smaller dipole moments immediately after the laser flash during the laser photolyses of BA and IA, respectively.

The decay of the MWDA signal in the case of BA is composed of fast and slow decay components on a time scales of a few hundreds nanosecond and a few tens of microsecond, respectively (Fig. 1b). The MWDA minus signal recovered to zero on a few hundreds of nanosecond time scale in the case of IA (Fig. 1c).

The amplitude of the MWDA signals in the case of BA increased to 120 and 145 in air- and oxygen-saturated benzene, respectively. The fast decay component was decelerated in air- and oxygen-saturated benzene. On the other hand, the amplitude of the MWDA signals in the case of IA increased to 48 and 78 in air- and oxygen-saturated benzene, respectively. The decay lifetime was more than a few microsecond.

Based on the experimental results, the photochemistry of BA and IA is different from that of CA in benzene. No study has been reported on the photochemistry of BA and IA, while homolytic cleavage of the C–X bond occurs to give a phenyl radical and X in the photochemistry of C<sub>6</sub>H<sub>5</sub>X. Similarly, the occurrence of homolytic cleavage of the C–X bond is suggested to give a *p*-aminophenyl radical and X in the photochemistry of BA and IA in benzene. The bond dissociation energies (BDE) of the C–X bonds are 95, 80, and 64 kcal mol<sup>-1</sup> for chloro-, bromo-, and iodobenzene, respectively [1,13]. The BDE of the C–Cl bond has been reported to be 85–91 kcal mol<sup>-1</sup> [1]. These results indicate that the order of the homolytic cleavage is CA < BA < IA because of the order of BDE, CA > BA > IA.

Formation of <sup>3</sup>IA\* and homolytic cleavage of the C–I bond occurs within a laser flash duration to give the *p*-aminophenyl radical and an iodine atom (I). This is consistent with the decrease in the dipole moment and the signal with an amplitude of –25. The recovery of the MWDA minus signal to zero in a few hundred nanosecond (Fig. 1c) corresponds to the radical recombination of radical pairs between the *p*-aminophenyl radical and I. The *p*-aminophenyl radical reacts with an oxygen molecule to give a *p*-aminophenyl peroxy radical on a few hundreds of nanosecond time scale in the presence of oxygen. This indicates a bimolecular rate constant in the order of 10<sup>8</sup>–10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> for the reaction of *p*-aminophenyl radical and oxygen [2].

The dipole moment ( $\mu$ ) of IA has been reported to be 2.89 D [9], while the  $\mu$  values of the *p*-aminophenyl radical and the *p*-aminophenyl peroxy radical were calculated to be 2.30 and 4.02 D, respectively, by the AM1 method using MOPAC Version 6 [8,11,12]. Because the *p*-aminoperoxy radical has a larger dipole moment than IA and the *p*-aminophenyl radical, the amplitude of the MWDA signal increases much more. The decay on a few tens of microsecond time scale can be explained by further reactions of the peroxy radical (Scheme 2).

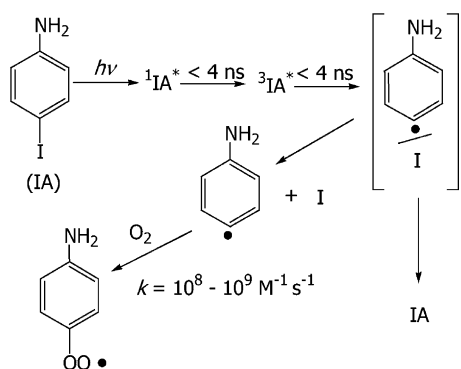
The dipole moment ( $\mu$ ) of BA has been reported to be 3.01 D [9], while a large  $\mu$  value is expected for the contact ion pair of [*p*-aminophenyl cation/Br<sup>-</sup>]. Observation of the large amplitude (93 mV) of the MWDA signal in the photo-

chemistry of BA, similar to 100 mV of the signal amplitude for an ion pair of aniline<sup>+</sup>/CCl<sub>4</sub><sup>-</sup> [8], suggests that the heterolytic cleavage of the C–Br bond in <sup>3</sup>BA\* occurs initially to give the contact ion pair of [*p*-aminophenyl cation/Br<sup>-</sup>] with a large dipole moment. However, the low yield of the heterolytic cleavage of the C–Cl bond in <sup>3</sup>CA\* and the lower electron negativity of Br than Cl suggest the lower yield of the heterolytic cleavage of the C–Br bond in <sup>3</sup>BA\*. Formation of this contact ion pair is probably explained by sequential electron transfer between the *p*-aminophenyl radical and Br in the contact radical pair generated from the homolytic cleavage of the C–Br bond in <sup>3</sup>BA\*, rather than the direct heterolytic cleavage of the C–Br bond in <sup>3</sup>BA\*.

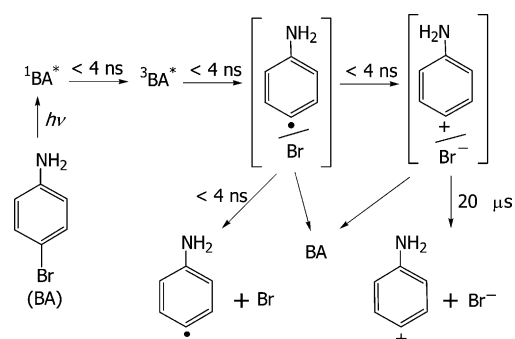
The fast decay on a few hundreds of nanoseconds time scale corresponds to recovery of BA through the recombination of two ions in the contact ion pair. The MWDA signal then decayed on a few tens of microsecond time scale and showed a minus value at 20  $\mu$ s. This indicates that a part of the contact ion pair dissociates into a free *p*-aminophenyl cation with a minus amplitude of the MWDA signal and Br<sup>-</sup>. Such a long lifetime (up to 20  $\mu$ s) of a contact ion pair of [aniline<sup>+</sup>/Br<sup>-</sup>] in non-polar solvents has been reported by Shimamori and Musasa [7]. The long lifetime of a few tens of microsecond is the specific property of contact ion pairs in non-polar solvents, while that in polar solvents is on a nanoseconds time scale.

The amplitude of the MWDA signals increased to 120 and 145 in air- and oxygen-saturated benzene, respectively, and the fast decay component was decelerated in air- and oxygen-saturated benzene. These results suggest that homolytic cleavage of the C–Br bond occurs partly to give a *p*-aminophenyl radical and a bromine atom (Br) (Scheme 3), and that the *p*-aminophenyl radical reacts sequentially with oxygen to give a *p*-aminophenyl peroxy radical having a larger dipole moment (Scheme 2).

Absorption spectra of the mixtures after irradiation of BA or IA in the presence of oxygen with more than a few tens of shots indicated peaks at 440–460 nm and 500 nm and were assigned to bromine (Br<sub>2</sub>) [14] and iodine (I<sub>2</sub>) [15], respectively. These results suggest that homolytic cleavages of C–Br and C–I bonds occur, at least partly, to give Br and I and Br<sub>2</sub> and I<sub>2</sub>, respectively.



Scheme 2.



Scheme 3.

### 3.3. Photochemistry of XA in benzene

The photochemistry of CA, BA, and IA in benzene is summarized in Scheme 4. Decay of  $^3\text{CA}^*$  having the ion pair character of a [*p*-aminophenyl cation/ $\text{Cl}^-$ ] occurs mainly, although it has been reported that the heterolytic cleavage of the C–Cl bond occurs in  $^3\text{CA}^*$  with a quantum yield of 0.03 in benzene based on the product analysis [1]. On the other hand, the homolytic cleavage of the C–I bond in  $^3\text{IA}^*$  is the main process. The homolytic cleavage of the C–Br bond occurs in  $^3\text{BA}^*$  to give a radical pair in which the electron transfer takes place to give the ion pair. The difference in the cleavage patterns is attributed to the character of the C–X bond in XA, and, the excitation energies ( $E_T$ ) of  $^3\text{XA}^*$ . BDE of the C–X bond are 95, 80, and 64 kcal mol $^{-1}$  for chlorobenzene, bromobenzene, and iodobenzene, respectively [1,13]. The BDE value of 85–91 kcal mol $^{-1}$  has been reported for CA [1]. The BDE of the C–X bond is expected to be in the order of CA > BA > IA; therefore, the efficiency of the homolytic cleavage of the C–X bond was in the order of CA < BA < IA. The  $E_T$  values of  $^3\text{CA}^*$ ,  $^3\text{BA}^*$  and chlorobenzene are 72, 76, and 82 kcal mol $^{-1}$ , respectively [16]. Although the  $E_T$  value of  $^3\text{IA}^*$  is not known, it is similar to the  $E_T$  of  $^3\text{CA}^*$  and  $^3\text{BA}^*$ .

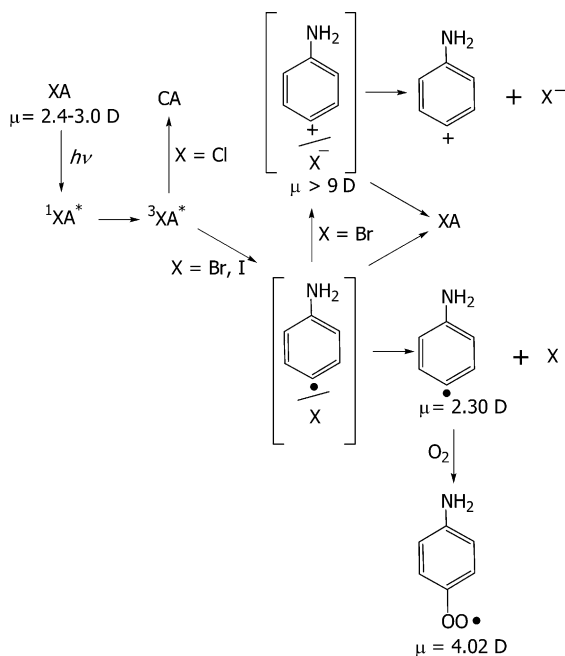
No homolytic cleavage has been explained by the lower  $E_T$  of  $^3\text{CA}^*$  than the BDE of the C–Cl bond of CA [1]. Decay of  $^3\text{CA}^*$  to CA takes place mainly, while heterolytic cleavage of the C–Cl bond in  $^3\text{CA}^*$  occurs in a low yield. The heterolytic cleavage is explained by  $^3\text{CA}^*$  having the ion pair character of [*p*-aminophenyl cation/ $\text{Cl}^-$ ]. The heterolytic cleavage does not occur or is not the major pathway in  $^3\text{BA}^*$  and  $^3\text{IA}^*$ , because the intramolecular charge-transfer character decreases in  $^3\text{BA}^*$  and  $^3\text{IA}^*$  compared with that in

$^3\text{CA}^*$  because of the electron negativity order of Cl > Br > I. Homolytic cleavage of the C–Br and C–I bonds in  $^3\text{BA}^*$  and  $^3\text{IA}^*$  occurs as a major process, because the  $E_T$  values of  $^3\text{BA}^*$  and  $^3\text{IA}^*$  are higher than the BDE of the C–Br and C–I bonds of BA and IA, respectively. In other words, the order of BDE relates to the stability of  $^3\text{XA}^*$  in the order of  $^3\text{CA}^* > ^3\text{BA}^* > ^3\text{IA}^*$ , and the efficiency of the homolytic cleavage in the order of CA < BA < IA. The electron transfer between the two radicals in the contact radical pair occurs considerably in the [*p*-aminophenyl radical/Br] to give the [*p*-aminophenyl cation/Br $^-$ ] but not in the [*p*-aminophenyl radical/I]. This difference is interpreted by the higher electron negativity of Br than I. We have also found reactions of  $^3\text{CA}^*$  having an ion pair character of a [*p*-aminophenyl cation/ $\text{Cl}^-$ ] with oxygen and a *p*-aminophenyl radical with oxygen with bimolecular rate constants of  $8.3 \times 10^7$  and  $10^8$ – $10^9$  M $^{-1}$  s $^{-1}$ , respectively. The one-order magnitude slower rate constant for  $^3\text{CA}^*$  is consistent with the ion pair character of [*p*-aminophenyl cation/ $\text{Cl}^-$ ].

These results are from the MWDA method which shows the time-variation of dipole moments of chemical species involving the photolysis of XA in benzene. The transient behavior of the  $^3\text{CA}^*$ , *p*-aminophenyl radical, *p*-aminophenyl peroxy radical, [*p*-aminophenyl cation/Br $^-$ ], and *p*-aminophenyl cation was discussed with respect to the MWDA signals during 308-nm laser photolyses of XA in benzene in the present study. Transient absorption measurement has been reported during the laser flash photolysis of only CA in polar solvents [1,2]. On the other hand, no transient absorption measurement has been reported for BA and IA. Transient absorption spectra of  $^3\text{CA}^*$  and the *p*-aminophenyl cation have been reported to show peaks at 450 and 430 nm with low absorption coefficients, respectively, in polar solvents. However, the transient behavior of  $^3\text{CA}^*$  is not clear because of overlapping of the absorption with the *p*-aminophenyl cation and further intermediates. Because the absorption of the [*p*-aminophenyl cation/Br $^-$ ] is considered to be similar to that of the *p*-aminophenyl cation, both cationic species cannot be distinguished. Radical species such as the *p*-aminophenyl radical and *p*-aminophenyl peroxy radical have absorption peaks with low absorption coefficients at shorter wavelengths than 300 nm which are not observed by the transient absorption measurement. Thus, the transient absorption measurement cannot function to clarify the mechanism involving such species. It is found that the MWDA method is useful to study the transient behavior of excited states, radicals, ions, radical pairs, or ion pairs with the independent dipole moments.

## 4. Conclusions

The photochemistry of CA, BA, and IA in benzene during 308-nm irradiation has been elucidated by the MWDA method in which the transient behavior of excited states and intermediates with independent dipole moments can



Scheme 4.

be detected. The product analysis is difficult because of the lower yields in non-polar solvents. Transient absorption measurement is not possible to clarify the mechanism, because excited states, radicals, and ions have relatively low absorption coefficients. In the present study we have elucidated the photochemistry of CA, BA, and IA in benzene from the time profiles of the MWDA signals. Formation of  $^3\text{CA}^*$  having an ion pair character of the [*p*-aminophenyl cation/ $\text{Cl}^-$ ], the [*p*-aminophenyl cation/ $\text{Br}^-$ ], and the *p*-aminophenyl radical took place immediately after the flash during laser irradiation of CA, BA, and IA in benzene. The yield of the cleavage of the C–X bond was in the order of  $\text{CA} < \text{BA} < \text{IA}$  which reflects the BDE order,  $\text{CA} > \text{BA} > \text{IA}$ . The decay of  $^3\text{CA}^*$  was observed with a lifetime of 3.8  $\mu\text{s}$ . The homolytic cleavage of the C–Br bond in  $^3\text{BA}^*$  occurs to give the [*p*-aminophenyl radical/ $\text{Br}^-$ ] which gives sequentially the [*p*-aminophenyl cation/ $\text{Br}^-$ ] through electron transfer between radicals. The dissociation of the [*p*-aminophenyl cation/ $\text{Br}^-$ ] to a *p*-aminophenyl cation and  $\text{Br}^-$  was observed to occur on a 20  $\mu\text{s}$  time scale. On the other hand, homolytic cleavage of the C–I bond in  $^3\text{IA}^*$  occurs efficiently to give a *p*-aminophenyl radical and I. Bimolecular reactions of  $^3\text{CA}^*$  having an ion pair character of the [*p*-aminophenyl cation/ $\text{Cl}^-$ ] with oxygen and *p*-aminophenyl radical with oxygen were found to occur at rate constants of  $8.3 \times 10^7$  and  $10^8$ – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. It should be emphasized that the MWDA method can be applied to elucidate the transient behavior of excited states, radicals, ions, radical pairs, or ion pairs with independent dipole moments during laser photolysis in non-polar solvents.

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