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Journal of Photochemistry and Photobiology A: Chemistry 195 (2008) 242–246
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photodissociation of bromochlorobenzenes

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Received 24 August 2007; received in revised form 8 October 2007; accepted 10 October 2007
Available online 17 October 2007

Abstract

The photodissociation kinetics of 2-, 3- and 4-bromochlorobenzene (BrClPh) and bromo-3,5-dichlorobenzene (Br-diClPh) have been studied in a molecular beam following excitation at 270 nm using femtosecond pump-probe spectroscopy. The kinetics and the dissociation dynamics in the BrClPhs were found to resemble the BrFPhs much more than the BrBrPhs. In 2- and 3-BrClPh two dissociation channels were observed, whereas 4-BrClPh and Br-3,5-diClPh dissociates via only one channel. The time constant for channel one, present in all molecules, depends on the number of chlorine atoms and their position. The absence of a second channel in 4-BrClPh is a general property among mixed Br-(Br, Cl or F)-Phs and is likely to be due to a dissociation channel involving a triplet excitation.

Keywords: Photodissociation; Substituent effects; Pump-probe spectroscopy; Molecular beam; Aryl halides

1. Introduction

Reaction dynamics of photo-induced chemical reactions is an important topic in modern physical chemistry. A thorough understanding of the excited state dynamics is essential for the possibility to actively intervene with and ultimately control the outcome of a chemical reaction. This is one reason why the photoreactions of alkyl halides and aryl halides have been widely studied in recent years both experimentally and computationally. In the alkyl halides the photoreaction consists of excitation directly to an anti-bonding state followed by an immediate dissociation. In the aryl halides the situation is more complex and interesting due to the presence of interacting bonding and anti-bonding states.

The absorption band of the aryl halides starts below 290 nm in the UV-region. The precise location depends on the nature of the substituents. In general, it corresponds to excitation of the first bound singlet state (S_1), and is referred to as the ^1L_b band. The photochemical properties of the ^1L_b band have been studied in a number of aryl halides using photofragment translational spectroscopy (PTS) [1–7], femtosecond time-resolved multi-photon ionization mass spectrometry (MPI-MS) [8–14] and *ab initio* methods [8,15–20]. In the simplest aryl halides, the mono halides, gas phase time-resolved MPI-MS measurements on iodo [9,11,13], bromo [11,13], and chlorobenzene [11,13] show that the lifetime after photo-excitation is strongly dependent on the nature of the halogen atom, 0.7, 30 and 1100 ps are reported for IPh, BrPh and ClPh, respectively. This has been taken as evidence for a model of photodissociation in the UV-region that consists of an excitation to the S_1 state, $\pi\pi^*$, localized on the aromatic ring, which couples to a repulsive triplet state (T_x), $^3n\sigma^*$ or $^3\pi\sigma^*$, this leads to photolysis of the carbon–halogen bond, i.e. the dissociation mechanism is based on a spin-orbit mediated singlet–triplet transition (S_1–T_x). In addition, a second very fast, dissociation channel has been observed in iodobenzene which is related to a direct excitation of a low lying repulsive singlet state, $^1n\sigma^*$, which is similar to the alkyl halides [21,22].

Aryl halides substituted with several fluorine [20,23], chlorine [4,14] and bromine [10,18] atoms and mixed halides [2,8,15,24] as well as halo toluenes [1,3,5,6,12,14,17] have also been investigated. Especially the bromobenzenes have been studied in a number of publications.

In dibromo- and tribromobenzenes, the S_1 lifetime was found to decrease with decreasing distance between the bromine atoms as well as with the number of bromine atoms. This dependence has been related to differences in spin-orbit coupling (SOC) [10,18]. Additionally, in two of the dibromobenzenes, 2- and 3-diBrPh, but not in 4-diBrPh, a second, smaller, time constant has been observed. *Ab initio* calculations show that the only

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doi:10.1016/j.jphotochem.2007.10.008

accessible singlet state at 4.59 eV (270 nm) is the S_1 state and a channel involving dissociation through the lower triplet states, only open in molecules of lower symmetry, has been proposed [18].

The photofragmentation of bromobenzenes substituted with lighter halogens is similar to the photofragmentation in bromobenzene in the meaning that it is typically the bromine atom that leaves the parent molecule. The SOC along the C–Br bound is not expected to be altered significantly by lighter halogens and a change in dissociation rate due to a substitution should thus be governed by other factors. The photodissociation of various bromofluorobenzenes was therefore recently investigated in a time-resolved MPI-MS/*ab initio* study [8]. The lifetime of the S_1 state changed with the position of the fluorine atoms in a more complex way than in the dibromobenzenes analogies, indicating that SOC effects are not dominating in this case. A second time constant was observed in 2-BrFPh and 3-BrFPh, but not in 4-BrFPh, in harmony with the dibromobenzenes. The dissociation in the polyfluoro-bromobenzenes, Br-2,6-diFPh and BrC_6F_5, was found to be different, with a sub-picosecond life time. This seems to be caused by a purely repulsive singlet state, mainly located along the C–Br bond that comes down in energy when the number of fluorine atoms increases. In the case of Br-3,5-diFPh the lifetime was found to be 1.9 ps, much longer than what would be expected from a direct excitation to a repulsive state. It is also shorter than what would be expected considering that *ab initio* calculations have shown that the height of the S_1–T_x barrier is not significantly lower in this molecule than in other bromobenzenes. In these calculations it was also conformed that there are no repulsive singlet accessible for direct dissociation. These findings led to some confusion about the reaction mechanism. A plausible solution was published in a recent computational paper [16] in which the out-of-plane bending of the Br atom was added to the previous model. This resulted in a lowering of the effective dissociation barrier, which subsequently will lead to a faster dissociation more in line with experiments. It very much highlights the limitations of using one dimensional potential energy curves (PEC) in detailed kinetic analysis of the dissociation processes in larger molecules.

In the present work, we investigate the influence of chlorine substitution on the photodissociation dynamics of bromobenzene. The molecules employed in this study are; 2-, 3-, 4-BrClPh and Br-3,5-diClPh.

2. Experimental

All chemicals were purchased from commercial retailers; 2-BrClPh from Lancaster Synthesis, 3-, 4-BrClPh and Br-3,5-diFPh from Sigma–Aldrich and used as received. The UV absorption spectra of the aryl halides, diluted with acetonitrile (typical concentrations of the solutes were 4×10^{-3} mol dm^{-3}), were measured using a conventional UV–vis spectrophotometer (Perkin Elmer Lambda 2).

The experimental arrangement for the time-resolved measurements consisted of an amplified Ti:sapphire femtosecond laser (Quantronix, 4800 fs 3k) with a repetition rate of 1 kHz and a pulse duration of about 150 fs, a molecular beam apparatus and a time-of-flight mass spectrometric detector (TOF-MS). It has been used in previous studies of aryl halides and is described in more detail elsewhere [10,25]. Briefly, the fundamental output from the regenerative amplifier was divided into two fractions using a beam splitter. One fraction was used to generate the 270 nm pump pulses by tripling the fundamental output using two BBO crystals, 1 and 0.4 mm thick. The other fraction was used to pump an optical parametric amplifier (TOPAS, Light Conversion), which generates the 547 nm probe pulses by sum and frequency mixing of the idler and the fundamental. The pump and probe beams were focused by a spherical plano-convex lens and spatially overlapped with the molecular beam inside the main chamber of the molecular beam apparatus. The relative polarization of the pump and probe pulses was kept at magic angle, 54.7°, by the mean of a Berek compensator. The molecular beam was provided by heating an oven with a 0.2 mm nozzle to 300–340 K depending on the vapour pressure of the compound. The nozzle was kept approximately 20 K higher in temperature in order to prevent condensation.

The UV pump excited the molecules and the probe ionized the excited molecules. After a flight distance of about 30 cm the ions were detected in a dynode-scintillator-photomultiplier arrangement. A boxcar integrator was used to select the desired ionic species by their arrival time. The lifetime of the excited state was determined by monitoring the yield of ions as a function of the delay time between the pump and the probe. An average of 1000 laser shots was recorded at each time point. Each time scan consisted of 80–160 time points and one measurement consisted of an average of typically 5–10 time scans.

Apart from ions produced by ionisation of molecules in the excited state, multiphoton ionisation from the ground state also occurred, giving rise to a small background signal. This signal is convenient to use for finding the best spatial overlap between the pump and the probe. It is proportional to the laser intensity and the amount of molecules in the beam and was also used for normalization purposes (see Section 3.1). In the time-resolved experiments low laser intensities were used in order to minimize contribution from this background signal (Fig. 3).

3. Results and discussion

The solution phase UV-absorption spectra all show the same main features and consist of a broad ^1L_a band at wavelengths shorter than 240–250 nm and a less intense ^1L_b band between 245 and 290 nm, Fig. 1. In all time-resolved measurements presented here we pump in the ^1L_b band. *Ab initio* calculations for Br_xPhs ($x = 1$, 2 or 3) [18], BrFPhs [8] and ClPh [17] show that the ^1L_b- and ^1L_a-bands correspond to a $\pi^* \leftarrow \pi$ transitions localized in the phenyl ring, and is identified as excitation to bound singlet states. Substituting one chlorine atom to bromobenzene should not influence the identity of the electronic states substantially compared to additional bromine or fluorine atoms.

The fragmentation pattern of the molecules can be seen in Fig. 2. These TOF-spectra were produced by multiphoton-excitation of the ground state molecules by the pump pulse alone using significantly higher intensities than in the time-resolved

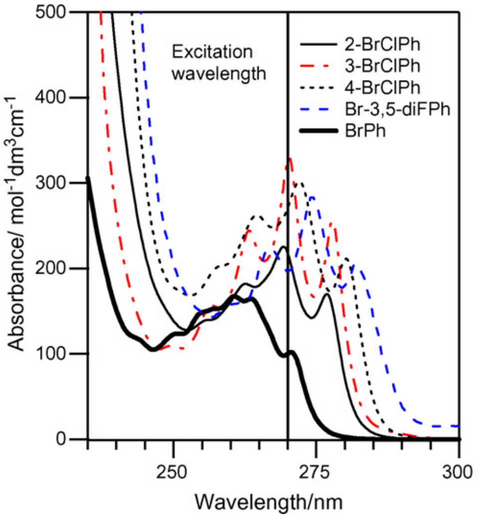

Fig. 1. UV absorption spectra of the investigated molecules in dissolved in acetonitrile, bromobenzene has been added to the figure as a reference. The pump energy is indicated with a vertical line.

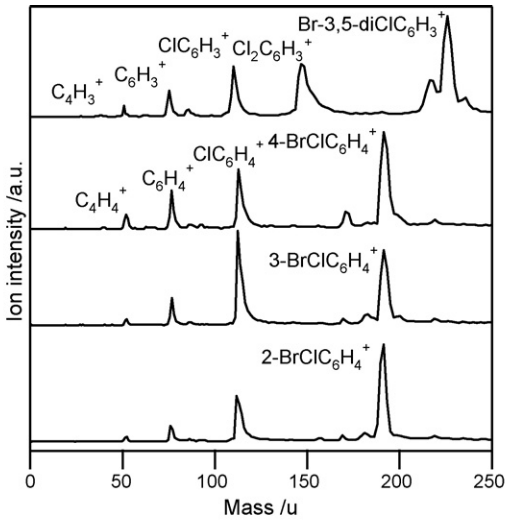

Fig. 2. Time-of-flight mass spectra recorded with the pump pulse alone at 270 nm. To illustrate the fragmentation pattern, the laser intensity was increased compared to the pump-probe experiments.

experiments. The main peak corresponds to the parent molecular ion and was the fragment selected to determine the kinetics of the excited molecules, presented in Fig. 3. In a few test runs we also measured the kinetics of the $ClC_6H_4^+$ fragments with the same results. This clearly shows that both the $ClC_6H_4^+$ ion and the molecular ion are produced from the same S_1 state and thereby reflect the same kinetics. It would be illustrative to also measure the dissociation products obtained in the photochemi-

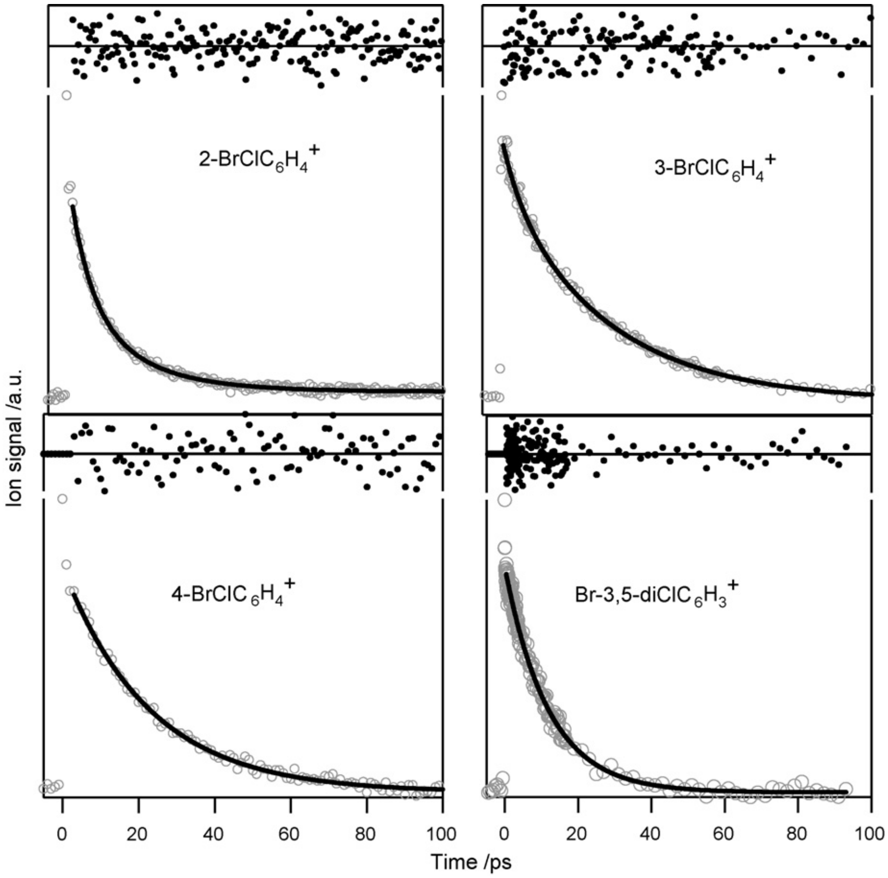

Fig. 3. Kinetic transients of the molecular ions, $BrClC_6H_4^+$ and Br-3,5-di$ClC_6H_3^+$. The open circles (○) represent the pump-probe signal, the thick solid line (—) represents the best-fit curve. Above each trace is the residual for the fit. The delay between pump and probe was increased until the ion signal reached a constant value. However, the same time scale has been used in all figures to illustrate the differences between the curves.

cal reaction. Unfortunately, this is not feasible with the present experimental set-up.

Kinetic traces of the bromochlorobenzenes showing the yield of parent ions, $BrClC_6H_4^+$ from bromochlorobenzene and $Br\text{-}diClC_6H_3^+$ from bromodichlorobenzene, as a function of the delay between pump and probe pulses are shown in Fig. 3. In addition to the pump-probe ion signal, the ion signal from the pump pulse was also recorded. The pump signal was subtracted from the pump-probe signal prior to the data analysis in order to correct for fluctuations of the laser intensity and variations in the density of the molecules in the molecular beam.

The ion signal, P, as a function of pump-probe delay, t, was fitted with an exponential decay function, $P = \sum_i A_i \exp(-\tau_i/t)$.

The number of exponentials, i, were increased until no significant improvement of the fit was seen. The best-fit parameters, τ_i and A_i, are summarized in Table 1. In order to obtain a good fit it was necessary to employ two time constants, τ_1 and τ_2, for 2- and 3-BrClPh while only one, τ_1, was required for 4-BrClPh and Br-3,5-diFPh. The samples contain several isotopes which may have slightly different dissociation kinetics. With the present signal-to-noise ratio the difference between the time constants has to be at least a factor of 2 in order to resolve them. Only one time constant was required for 4-BrClPh and Br-3,5-diFPh, hence the isotope effects have to be small and from that aspect a single exponential decay is expected for all molecules investigated here. The result that two time constants are necessary in the 2-, and 3- isomers but not in the 4-isomer has previously been observed for 2-, 3-, 4-BrXPh [8,10,18] (X = Br or F) and seems to be a general property in this family of molecules when pumping with 270 nm. The presence of two time constants implies that two different excited electronic states, with separate dissociation mechanisms, are involved. These mechanisms will be discussed separately starting with the slower one designated τ_1.

3.1. The photodissociation mechanism via S_1–T_x

The time constants for dissociation associated with the slower channel, τ_1, for 2-, 3-, 4-BrClPh and Br-3,5-diClPh are presented together with eight other bromine containing aryl halides in Fig. 4 [8,10,18]. The time constants are correlated with the total molecular mass, but also slightly dependent on the relative position of the halogen atoms.

The correlation between molecular mass and time constant could be taken as an indication that the same dissociation mechanism prevails in all these molecules, i.e. dissociation via the S_1–T_x channel. Recent studies on substituted bromobenzenes [8,10,12,18] show that molecules that significantly deviate from this correlation have a different dissociation mechanism, e.g. the polyfluorobromobenzenes. Also *ab initio* calculations [8,18] of the PECs along the C–Br bond in bromofluorobenzenes and polybromobenzenes have verified that the repulsive states come down in energy when introducing additional substituents, resulting in a lower predissociation barrier. In a similar manner, additional chlorine atoms are expected to lower the predissociation barrier also in the present molecules, resulting in a shorter S_1 lifetime in line with the experimental findings.

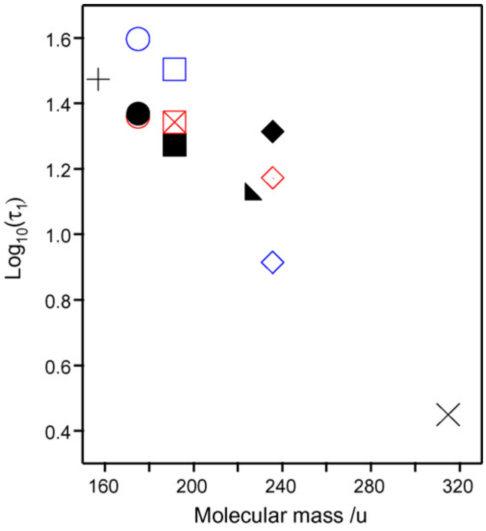

Fig. 4. The S_1-lifetime of 11 bromine containing aryl halides, BrPh (+), 2-, 3-, 4-BrFPh (○, ⊗, ●), 2-, 3-, 4-BrClPh (□, ☒, ■), 2-, 3-, 4-BrBrPh (◇, ⟐, ◆), Br-3,5-diClPh (◣) and 1,3,5-triBrPh (×) plotted as a function of total molecular mass.

In addition, having several halogen atoms introduces the possibility for additional dissociation channels. This has been shown by the group of Das [26] who has observed production of both chlorine and iodine atoms after excitation of chloroiodobenzenes at wavelengths shorter than 280 nm. Accordingly, chlorine atoms may also be produced in bromochlorobenzenes. A rough estimation of the effect of additional dissociation channels on the S_1 lifetime in bromobenzene could be realized from the S_1 lifetime in dichlorobenzene. In a gas phase time-resolved MPI-MS experiment, exciting 4-diClPh with 270 nm, Yuan *et al.* measured the S_1 lifetime to be 122 ps [14]. This corresponds to having two dissociation channels with lifetimes of 244 ps each. Compared to bromobenzene, a second chlorine channel out from the S_1 state with a time constant of say 200 ps would lower the S_1 lifetime from 36 ps[1] to 31 ps and similarly two such additional channels would result in a S_1 lifetime of 26 ps.

Considering the position effect in the di-substituted aryl halides, the S_1-lifetime increases from 18.6 and 22.1 ps for 2-BrClPh and 4-BrClPh to 32.5 ps for 3-BrClPh. This relation

Table 1
Best-fit parameters for pump-probe data, the amplitudes have been normalized to unity

Molecule	A_1	τ_1 (ps)	A_2	τ_2 (ps)
$BrC_6H_5^{+a}$	1	30 ± 2	–	1.1 ± 0.2[b]
$ClC_6H_5^{+a}$		1100		0.4 ± 0.1[b]
$2\text{-}BrClC_6H_4^+$	0.4	18.6 ± 1.6	0.6	5.8 ± 1.0
$3\text{-}BrClC_6H_4^+$	0.6	32.5 ± 2.4	0.4	10.6 ± 4.7
$4\text{-}BrClC_6H_4^+$	1	22.1 ± 2.1	–	–
$Br\text{-}3,5\text{-}diClC_6H_3^+$	1	11.4 ± 0.9	–	–

[a] Measured at 266 nm by Kadi *et al.* [11].
[b] The fast decay component is due to rotational dephasing.

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[1] In Table 1 the dissociation time constant for BrPh is reported to be 30 ps when exciting with 266 nm. Unpublished measurements exciting with 270 nm results time constant of 36 ps.

resembles the bromofluorobenzenes more than dibromobenzenes, which indicates that the primary effect on the dissociation dynamics when adding chlorine atoms is not to increase the SOC between the S_1 and T_x states. Hence the predissociation barrier must be lowered by some other mechanism. Since the previously calculated one dimensional PECs along the C—Br bond for 2-, 3- and 4-BrFPh show no clear correspondence between the energy of the different S_1–T_x crossing points and the S_1 lifetimes [8]. Additional dimensions are required to capture the details of the dissociation dynamics.

3.2. The second channel, τ_2.

The absence of a second channel in para substituted bromobenzenes has previously been reported for both BrFPh and diBrPh [8,10]. The PECs along the C—Br bond in 2-, 3-, 4-diBrPh and 2-, 3-, 4-BrFPh are very similar in comparison [8,18] and it is thus likely that the same situation prevails also in 2-, 3-, 4-BrClPh. In the Br–X–Phs, there are four bound states within reach at 270 nm, one singlet state and three triplet states. One of the triplet states close in energy to the singlet state is likely to be populated. In 2- and 3-BrXPh, excitation of a triplet state could result in dissociation via a low lying barrier while the triplet state in 4-BrXPh is bound at the present energies due to a higher symmetry in the para position, we refer to Refs. [8] and [18] for thorough discussions on the symmetry effect.

4. Conclusions

The photodissociation kinetics of 2-, 3-, 4- bromochlorobenzene is found to be more similar to kinetics of the bromofluorobenzenes than the dibromobenzenes. In 2- and 3-BrClPh two different dissociation channels were found, whereas only one channel was found in 4-BrClPh and Br-3,5-diClPh. For the slower channel, which is present in all molecules, the time constant was dependent on the position and the number of chlorine atoms. The latter is probably an effect of lowering the repulsive states and introducing additional C—Cl dissociation channels. The position effect was found to be more irregular than in the dibromobenzenes with the largest time constant found in 3-BrClPh. To obtain a solid understanding an extensive theoretical investigation has to be undertaken.

The presence of a second channel only in the 2- and 3- isomers seems to be a general property among mixed Br–Y–Phs (Y = Br, Cl or F). This channel is attributed to a mechanism involving an initial excitation of a low lying triplet state with a minor barrier for dissociation, not present in the para substituted molecules due to the change in symmetry.

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