π-Complexes as "Modulators" of Bromine Atom Reactivity in Solution

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Introduction

It is well-established that halogen atoms form π-molecular complexes with aromatic solvents,[1] in which the aromatic compound acts as an electron donor and the halogen atom as an electron acceptor, and hence the π-complex has a certain charge-transfer character. Formation of halogen atom/aromatic molecular complexes has been shown to influence significantly the selectivity and reactivity of reactions such as free-radical chlorination.[2]

Very few equilibrium constants for these complexes have been determined.[2,3] Furthermore, in contrast to the case of chlorine atoms, and of reactions in the gas phase, there are only a handful of reports on absolute rate constants for hydrogen abstraction by bromine atoms in solution.[4−8] The work described herein focuses on a quantitative analysis of bromine atom/aromatic π-complex formation and its effect on the reactivity of hydrogen abstraction by bromine atoms in solution.

Results and Discussion

Bromine atoms are generated upon photochemical dehalogenation of α-bromoacetophenone. In neat benzene, bromine atom/benzene π-complex formation leads to an absorption band centered at 550 nm (Figure 1), in excellent agreement with literature values.[9] However, as the polarity of the medium increases, a hypsochromic (blue) shift of the wavelength of maximum absorption (λ_{max}) is observed (e.g., λ_{max} 530 and 510 nm in acetonitrile/benzene 82:18 v/v and 99:1 v/v, respectively). This hypsochromic shift suggests that solvation of the π-complex in the ground state would result primarily from localized interactions with the uncharged component species, rather than from the dipole due to the contribution from the charge-transfer structure, as indeed observed in the case of several charge-transfer complexes formed from neutral species.[10] Interestingly, no significant shift could be detected in the λ_{max} corresponding to chlorine atom/benzene π-complexes when working under the same conditions (Figure 1).

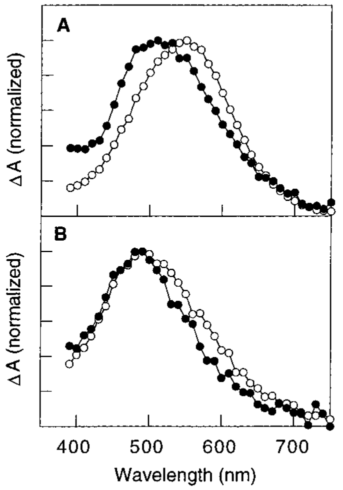

Figure 1. Transient absorption spectra for halogen atom/benzene complexes recorded upon 355-nm laser excitation of α-bromoacetophenone (A) and α-chloro-acetophenone (B) in benzene (○) and in 9:1 (v/v) acetonitrile:benzene (●) solutions.

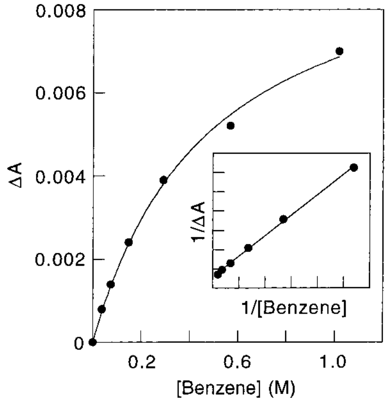

Figure 2. Dependence of the change in relative absorbance for bromine atom/benzene π-complex as a function of benzene concentration. Inset: double reciprocal plot.

Formation of bromine atom/aromatic π-complexes takes place instantaneously (i.e., within the time resolution of our system ca. 20 ns). When the signal intensity (ΔA) corresponding to π-complexes in acetonitrile solution is recorded as a function of the concentration of aromatic species (such as chlorobenzene, benzene, and *tert*-butylbenzene) a nonlinear dependence is observed (Figure 2 is representative). The double reciprocal plots are indeed linear (Figure 2, inset) in agreement with a 1:1 interaction. Nonlinear fittings of ΔA values vs concentration of aromatic species according to the well-known Benesi−Hildebrand equation[11] lead to values of equilibrium constants for π-complex formation (K_{eq}) of (0.8 ± 0.2), (2.2 ± 0.3), and (4.6 ± 0.8) M^{-1} for chlorobenzene, benzene, and *tert*-butylbenzene, respectively. These K_{eq} values agree very well with those determined from the ratio between the intercept and the slope of the double-

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Table 1. Second-Order Rate Constants (k_H) for Hydrogen Abstraction by Bromine Atoms in Various Solvents

	$k_H{}^a$ (10^6 M^{-1} s^{-1})			
H-donor	CH_3CN^b	$CH_3CN/C_6H_6{}^c$ 9:1 v/v	$CH_3CN/t\text{-}BuC_6H_5{}^c$ 9:1 v/v	$C_6H_6{}^c$
methanol	1.6 ± 0.8 (1.0)	0.49 ± 0.02 (1.6)	0.44 ± 0.02 (1.6)	*d*
diethyl ether	24 ± 1 (0.14)	6.4 ± 0.2 (0.45)	5.6 ± 0.4 (0.16)	0.46 ± 0.03 (0.90)
2-propanol	32 ± 3 (0.05)	9.0 ± 0.3 (0.5)	8.5 ± 0.2 (0.25)	0.54 ± 0.04 (1.2)
toluene	70 ± 6 (0.025)	19.5 ± 0.6 (0.055)	17.4 ± 0.5 (0.06)	0.64 ± 0.03 (0.85)

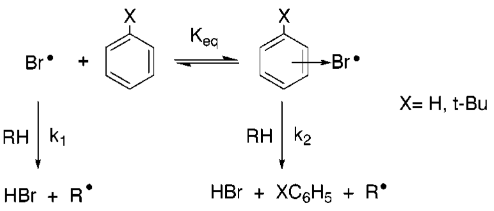
[a] Maximum molar concentration of H-donor used given in parentheses. [b] $Br_2{}^{\bullet-}$ as probe. [c] π-Complex as probe. [d] Reaction was too slow to determine an accurate value.

reciprocal plots. The changes observed in K_{eq} values as a function of the type of aromatic π-donor are interpreted in terms of electronic effects (i.e., K_{eq} increases in the presence of an electron-donating group such as *t*-Bu, whereas a decrease is observed in the presence of an electron-withdrawing group such as Cl). Not surprisingly, K_{eq} values are solvent dependent, and solvent effects can be interpreted in terms of a balance between the ionizing power and the complexation ability of the solvent. For benzene π-complex formation, K_{eq} in cyclohexane (a less ionizing solvent than acetonitrile) is found to be (1.4 ± 0.2) M^{-1}, whereas in dichloromethane (complexing solvent)[12] the plot (not shown) of ΔA vs benzene concentration ([benzene] $\le$ 1 M) is essentially linear, indicating $K_{eq} \le 0.1$ M^{-1}. This observation is in good agreement with the value reported for bromine atom/benzene π-complex formation in carbon tetrachloride (i.e., 0.2 M^{-1}).[3]

Observed bromine atom reactivity (k_{obs}) was determined by means of laser-flash photolysis, using the probe technique[13] based on the formation of detectable complexes between bromine atoms and (i) aromatic compounds (π-complex) or (ii) bromide anions ($Br_2{}^{\bullet-}$). The latter are characterized by having a strong absorption band centered at 360 nm.[14] In the presence of 10% (v/v) benzene or *tert*-butylbenzene in acetonitrile, no change could be detected in the second-order rate constant for formation of $Br_2{}^{\bullet-}$ (i.e., $(2.1 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1}), which indicates that the reactivity of "free" and complexed bromine atoms toward bromide anions in acetonitrile solution are rather similar (i.e., diffusion controlled). In neat benzene, the second-order rate constant for formation of $Br_2{}^{\bullet-}$ is $(3.4 \pm 0.2) \times 10^9$ M^{-1} s^{-1}.

Rates of hydrogen abstraction by bromine atoms were determined by monitoring either the buildup at 390 nm ($Br_2{}^{\bullet-}$ as probe) or the decay signal at 510 nm (π-complex as probe) as a function of H-donor concentration ([RH]). In all cases, second-order rate constants (k_H) were obtained from the slopes corresponding to the linear plots (not shown) of k_{obs} vs [RH]. Resulting values are summarized in Table 1. Not surprisingly, the reactivity of bromine atoms decreases in the presence of aromatic compounds.

Scheme 1



In the presence of 10% (v/v) benzene or *tert*-butylbenzene in acetonitrile solution, the second-order rate constant k_H for H-abstraction can be related to the equilibrium constant for π-complex formation (Scheme 1) according to eq 1.

$$k_H = \frac{k_1}{1 + K_{eq}[XC_6H_5]} + \frac{k_2 K_{eq}[XC_6H_5]}{1 + K_{eq}[XC_6H_5]} \qquad (1)$$

The values of k_H determined in acetonitrile solution using $Br_2{}^{\bullet-}$ as probe correspond indeed to k_1, and are in excellent agreement with data in the literature.[7] The values of k_H determined in benzene solution, on the other hand, do not necessarily correspond to the reactivity of the 1:1 π-complex, since in neat benzene complexes of higher stoichiometry may most likely exist.[15] The decrease in reactivity in the presence of aromatic solvents clearly indicates that k_2 is significantly lower than k_1. Assuming the second term of eq 1 to be negligible for 9:1 (v/v) acetonitrile/benzene and acetonitrile/*tert*-butylbenzene solutions, one obtains $k_H/k_1 = (1 + K_{eq}[C_6H_6])^{-1}$. From the ratio k_H/k_1, K_{eq} values of (2.3 ± 0.4) M^{-1} and (4.6 ± 0.6) M^{-1} are calculated for benzene and *tert*-butylbenzene, respectively, in excellent agreement with K_{eq} values determined from absorption data (vide supra). These results support the assumption that the second term of eq 1 is negligible and clearly show that aromatics act as modulators of bromine atom reactivity by controlling bromine atom concentration via complexation.

When toluene is used as H-donor in acetonitrile solution, at [toluene] > 0.01 M the corresponding π-complex can be detected immediately after laser excitation. In fact, bromine atom/toluene π-complex can be detected even in neat toluene ($\lambda_{max} = 535$ nm, spectrum not shown) with a lifetime of 172 ns. The latter is in very good agreement with the lifetime estimated from the second-order rate constant measured in neat benzene, i.e., $1/(6.4 \times 10^5$ M^{-1} $s^{-1} \times 9.39$ M$)$ = 166 ns. Alternatively, if an intramolecular H-abstraction were to take place within toluene π-complex, the second-order rate constants shown in Table 1 for acetonitrile and benzene solutions would represent the product between the corresponding equilibrium constant for bromine atom/toluene π-complex formation (assumed to be similar to that for *tert*-butylbenzene π-complex) and the first-order rate constant for intramolecular H-abstraction. A first-order rate constant of 1.5×10^7 s^{-1} results from data in acetonitrile (K_{eq} = 4.6 M^{-1}), whereas a value lower than 6.4×10^5 s^{-1} (and, consequently, a lifetime of the order of microseconds) would result from data in neat benzene. Since hydrogen abstraction rates for bromine atoms seem to be largely unaffected by the polarity of the solvent,[8] the (at least) 23-fold change in first-order rate constant contradicts an intramolecular process. However, the decrease in reactiv-

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ity observed when the solvent is changed from acetonitrile to benzene agrees very well with a change in reactive species, i.e., from “free” (reactive) to complexed (less reactive) bromine atoms. Thus, it is inferred that in the case of toluene H-abstraction *does not* take place within the corresponding π-complex, but rather toluene acts both as a reactant and, as in the case of the other aromatics employed in this study, as a modulator of bromine atom reactivity via complexation.

Experimental Section

Acetonitrile, benzene, methanol, 2-propanol, and toluene (BDH Omnisolv), *tert*-butylbenzene (Aldrich), and tetrabutylammonium bromide (Across) were used as received. Diethyl ether (BDH ACS) was distilled before use. α-Bromoacethophenone (Across) and α-chloroacethophenone (BDH) were recrystallized from aqueous ethanol and hexane, respectively, before use.

Laser experiments were carried out using a Q-switched Nd:YAG laser (Continuum, Surelite I) operated at 355-nm (4−6 ns pulses, <30 mJ/pulse) for excitation. The system is controlled by a Power Macintosh 7100/80 computer running LabVIEW 3.1.1 from National Instruments. This computer is interfaced (GPIB) to a Tektronix TDS 620 A digitizer used for data acquisition. Other aspects of this laser system have previously been described.[16,17] Solutions were contained in quartz cells constructed of 7 × 7 mm^2 Suprasil tubing. All measurements were performed at 21 °C using air-equilibrated samples.

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Supporting Information Available: Plots of signal intensity (ΔA) for bromine atom/aromatic π-complexes as a function of the concentration of aromatic species; observed bromine atom reactivity as a function of H-donor concentration; transient spectra recorded in neat toluene. This material is available free of charge via the Internet at http://pubs.acs.org.

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