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Flash Photolysis of 1,4-Dibromobenzene and 4-Bromobiphenyl in Benzene. Cyclohexadienyls as Intermediates in Free Radical Arylations

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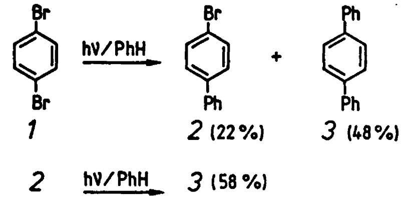
Photolysis of 1,4-dibromobenzene in benzene produces 4-bromobiphenyl and *p*-terphenyl and photolysis of 4-bromobiphenyl produces *p*-terphenyl. These products were shown by flash photolysis to be formed *via* cyclohexadienyl radicals. The visible absorption of these radicals, which decayed in a second order reaction, could be traced to 500 nm. The ratio of second order rate constants in benzene-h_6 and benzene-d_6, k_H/k_D, was calculated as $1.8 \pm ca.$ 0.4 for 1,4-dibromobenzene and $1.5 \pm ca.$ 0.4 for 4-bromobiphenyl. Quenching studies showed that 1,4-dibromobenzene photolysed mainly from the triplet state (75 %) while 4-bromobiphenyl photolysed exclusively from the triplet state.

The primary step in the photolysis of simple aryl halides is homolysis of the carbon-halogen bond.[1] Since nonreversible, fast addition of alkyl and aryl radicals to benzene produces cyclohexadienyls [2,3] this system may be observed by flash photolysis of aryl halides in benzene solution. In this study the photochemical properties of two bromine containing aromatic compounds, 1,4-dibromobenzene (*1*) and 4-bromobiphenyl (*2*) were investigated.

RESULTS

Steady-state photolysis of 1,4-dibromobenzene and 4-bromobiphenyl. Compound *1* (Scheme 1), 1.5×10^{-3} M in benzene solution deaerated with argon, was photolysed through quartz to give compound *2* (22 %) and *p*-terphenyl (*3*, 48 %). Photolysis through pyrex ($\lambda > 300$ nm) was ineffective (see Experimental).



Scheme 1.

Similarly, compound *2*, 1.4×10^{-3} M in benzene, was photolysed to give *3* (58 %).

Flash photolysis of compound 1. Flash photolysis of compound *1* (5×10^{-4} M) in degassed benzene permitted the observation of a transient absorption decaying in a second order reaction (Fig. 1). The half-life of the signal was 0.7 ms. The intensity increased gradually from 500 nm to the limit of detection at 350 nm ($A_{400} = 0.002$). If an air-saturated benzene solution was flashed, the half-life of the signal was unchanged, but its intensity was less (1/4). The kinetics of the reaction in the presence of oxygen was complex, being neither of first nor of second order.

The intensity of the flash signal was also reduced upon addition of 1,3-pentadiene (piperylene) under oxygen-free conditions. Thus, at 10^{-2} M 1,3-pentadiene the intensity of the signal had decreased to 1/3 of its original value and the half-life had increased three times (from 0.7 to 2.0 ms, in agreement with second order kinetics*). The intensity did not decrease

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* For second order reactions in which the starting concentrations of the two reactants are identical, $t_{\frac{1}{2}} = 1/kc_0$.

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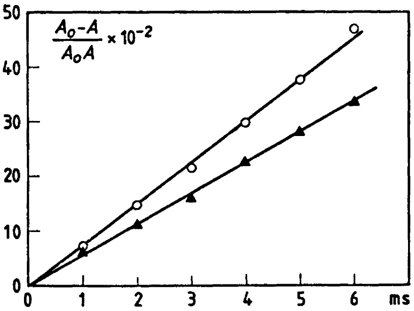
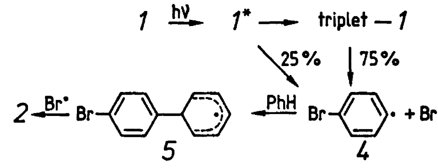


Fig. 1. Second order plots of oscilloscope traces at 400 nm. A_0 is the initial intensity, in absorbance. ○, 1,4-Dibromobenzene (*1*), 4.1×10^{-4} M in degassed benzene, correlation coefficient of the plot (r) 0.9988. ▲, 4-Bromobiphenyl, 5.0×10^{-4} M in degassed benzene, $r=0.9996$.

upon further addition of pentadiene. Addition of small amounts of bromine, which is photolysed during the flash to give bromine atoms, caused the half-life of the signal to decrease from 0.7 to 0.2 ms, under oxygen-free conditions. The initial intensity of the signal (A_0) was unchanged. This rate effect was also observed with aerated solutions. Furthermore, in the presence of bromine, the signal decayed in a first order reaction.

The effect of the addition of bromine might be due to hydrogen abstraction from the intermediate observed. An isotope effect might therefore be found if decay rates are measured in C_6H_6 and C_6D_6. For second order reactions $c_0t_{\frac{1}{2}}$ must be constant ($=1/k$) at constant temperature. Since absorption coefficients are not known, A_0 was measured at 400 nm and the product $A_0t_{\frac{1}{2}}$ calculated. One must, therefore, assume that absorption coefficients are not significantly different in C_6H_6 and C_6D_6 and that $A_0=\varepsilon c_0l$ (the Lambert-Beer law). Values of $t_{\frac{1}{2}}$ were calculated from plots analogous to those shown in Fig. 1. Two determinations of the product $A_0t_{\frac{1}{2}}$ in C_6H_6 at 24.5 °C gave the values 3.3×10^{-7} and 3.9×10^{-7} s. In C_6D_6 at 24.5 °C two determinations gave the value 6.5×10^{-7} s. k_H/k_D is therefore calculated as $6.5/3.6=1.8\pm$ *ca.* 0.4.

From these experiments we conclude (see Discussion) that the observed transient is a free radical which is formed from both the excited singlet and triplet state of *1* as indicated by the effect of oxygen and 1,3-pentadiene. The radical is suggested to be the cyclohexadienyl *5* (Scheme 2).

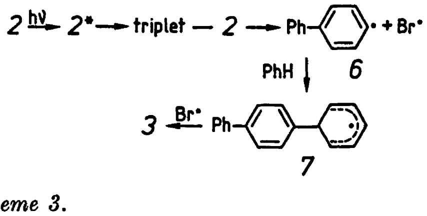


Scheme 2.

Flash photolysis of compound 2. By flash photolysis of *2* in degassed benzene (5×10^{-4} M) an intermediate decaying in a second order reaction was observed (Fig. 1). The initial intensity of the signal, the half-life and the spectrum were nearly identical with those observed by flash photolysis of compound *1*. By addition of 10^{-5} M bromine the half-life of the signal (A_0 unchanged) decreased from 0.7 to 0.4 ms and the decay was no longer of second order. Pseudo first order kinetics was observed from $t=0$ to $t=0.8$ ms ($2\times t_{\frac{1}{2}}$). Significant deviation from first order kinetics ("tailing" of the signal) was observed at $t>0.8$ ms.

In C_6H_6 two calculations of $A_0t_{\frac{1}{2}}$ gave the values 1.2×10^{-6} s and 1.3×10^{-6} s, respectively (26.7 °C). In C_6D_6 the values 1.7×10^{-6} and 2.0×10^{-6} s were estimated at 26.6 °C. k_H/k_D is therefore calculated as $1.5\pm$ *ca.* 0.4. The intermediate is suggested to be the cyclohexadienyl *7* (Scheme 3, see Discussion).

The photoreaction of *2* was completely quenched by 10^{-3} M 1,3-pentadiene, indicating that only the triplet state of compound *2* is photoactive. This triplet was observed in degassed benzene solution as an intense, short-lived absorption between 425 and 500 nm, decaying in a first order reaction with $k=1.7\times10^4$ s^{-1}. In the presence of oxygen only a very weak signal was detected. Its decay rate was unaffected by addition of bromine.



Scheme 3.

DISCUSSION

The primary step in the photolysis of simple aryl halides, when nucleophilic reagents are absent, is homolysis of the carbon–halogen bond. This reaction has been investigated by gas-phase flash photolysis of a number of mono- and disubstituted halobenzenes.[1] The phenyl radicals so formed showed weak absorptions in the region 400–600 nm. In aqueous solution phenyl radicals were also found to absorb at 260 nm.[4] In liquid solution both relative and absolute reactivities toward different substrates have been measured. Thus, the second order rate constant associated with the addition of phenyl radicals to benzene is 1.0×10^6 M^{-1} s^{-1} (Ref. 3). The lifetime of phenyl radicals generated in benzene is therefore approximately 10^{-7} s. The intermediates identified in this study are therefore not substituted phenyl radicals. This can also be concluded from the kinetics of the reactions, since absorptions of phenyl radicals, generated in benzene, must decay in a pseudo first order process. Phenyl radicals do not dimerize to any significant extent in solution.[3]

The addition of the phenyl radical to benzene produces the phenylcyclohexadienyl radical.[3] The absorption spectrum of this radical seems to be unknown. However, the electronic absorption spectrum of the parent compound, the cyclohexadienyl radical, has been recorded at room temperature in an adamantane matrix [5] and at 77 K in a methanol glass.[6] It exhibits structured absorptions at *ca.* 310 and 550 nm. The latter bands are weak.

The α-hydronaphthyl radical absorbs at 530 nm.[6]

The evidence for assigning structures *5* and *7* to the intermediates is as follows: Phenyl radicals are trapped very fast by the solvent benzene (the half-life of phenyl radicals in benzene is 10^{-7} s, see above. The lifetime of the flash is *ca.* 5×10^{-5} s). The photolysed sample should therefore contain equal amounts of bromine atoms and substituted cyclohexadienyl *5* or *7* just after the flash. In degassed solution the intermediates are consumed in simple second order reactions (Fig. 1, $\mathrm{d}A/\mathrm{d}t=k'A^2 \Rightarrow (A_0-A)/A_0A=k't$. Absolute values of rate constants cannot be estimated since absorption coefficients are unknown). Since no dimerization or disproportionation products were isolated in the preparative experiments, this reaction order is probably due to hydrogen abstraction from the intermediates by the bromine atoms generated in the primary photochemical step (Schemes 1 and 2). This mechanism was rendered probable by the effect of addition of small amounts of bromine to the photolysis mixture and by measurement of isotope effects. Added bromine dissociates during the flash. The hydrogen abstraction process should, therefore, be accelerated and pseudo first order kinetics should be observed at relative high concentrations of bromine atoms. These predicted effects of added bromine were observed. In the presence of oxygen the intermediate assigned as *5* was also consumed faster, as indicated by the decrease of the initial intensity (four times, due to quenching of the triplet state of *1*) but unchanged half-life. *5* is probably converted into *2* both by bromine and by oxygen simultaneously, since the kinetics of the reaction was neither of first nor of second order.

The magnitude of the primary isotope effect in hydrogen atom transfer reactions is influenced by bond dissociation energies. Large isotope effects are associated with small values of ΔH.[7,8] Thus, the deuterium isotope effect for the reaction $X\cdot+PhCH_3\rightarrow HX+PhCH_2\cdot$ is $k_H/k_D=6.7$ for X=Br ($\Delta H_0=-3$ kcal/mol) and 1.8 for X=Cl ($\Delta H_0=-18$ kcal/mol).[8,*] The bond dissociation energy of the two reactive carbon–hydrogen bonds in the cyclohexadienyl radical is as low as 27 kcal/mol.[9] The bond dissociation energy of hydrogen bromide is 87 kcal/mol.[10] The hydrogen abstraction from *5* and *7* by atomic bromine is therefore exothermic by ~60 kcal/mol. The hydrogen transfer will be less than half-complete at the transition state [7] and kinetic isotope effects will be small.

Alternatively, one might assume that the decay process observed by flash photolysis is an addition reaction. If atomic bromine adds to a carbon-carbon double bond in *5* or *7*, a small, secondary isotope effect might be found. However, in addition reactions to double bonds, deuterium substitution will *increase* the rate (inverse isotope effect).[11] The proposed mechanism is therefore in agreement with the estimated kinetic isotope effect.

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[*] 1 kcal = 4.184 kJ.

The parent cyclohexadienyl absorbs at 550 nm (see above). The cyclohexadienyls *5* and *7* might well absorb at longer wavelength. However, when benzene solutions of compounds *1* and *2* are flashed, most of the flash light will be absorbed by the solvent. Hence, signals will be relatively weak and only the more intense parts of the spectra of *5* and *7* can be observed. In this study the absorption of the intermediates could be traced to 500 nm.

The effect of oxygen and 1,3-pentadiene on the initial concentration of the radicals formed indicate that photolysis takes place *via* the triplet state.[12] However, the observed effect could be due to reaction of initially formed aryl radicals with oxygen or piperylene.[3] Since the concentration of *5* is not further decreased at piperylene concentrations above 10^{-2} M the latter mechanism cannot be important. The results of the quenching experiments are summarized in Schemes 2 and 3.

EXPERIMENTAL

Compounds. 1,4-Dibromobenzene (*1*) and 4-bromobiphenyl (*2*) are commercially available. Compound *1* was recrystallized twice from methylcyclohexane and compound *2* from methanol. UV absorption data in cyclohexane are: Compound *1*, λ_{max} 282 nm, ε 260 M^{-1} cm^{-1}, $\varepsilon_{300} \sim 0$ M^{-1} cm^{-1}. Compound *2*, λ_{max} 256 nm, ε 22 000 M^{-1} cm^{-1}, $\varepsilon_{300} \sim 200$ M^{-1} cm^{-1}. The benzene used was analytically pure.

Flash photolysis. The flash lamp (quartz) was filled with air and the light was filtered with aqueous NaBr ($\lambda > 230$ nm). Flash energies were 200 J. The analysing light beam was passed through a monochromator, through the reaction cell and through a second monochromator with a photomultiplier on the exit slit. Decay curves were stored by means of a Tektronix 549 oscilloscope.

*Steady-state photolysis of 1,4-dibromobenzene (*1*) and 4-bromobiphenyl (*2*).* Compound *1* (0.52 g) was dissolved in benzene (1.50 l) and photolysed for 18 h through quartz using external medium pressure mercury lamps (3 000 W). Prior to and during photolysis argon was bubbled through the solution. The photolysis mixture was cooled using a heat exchanger of steel, cooled with tap water. After evaporation, the residue was separated by preparative layer chromatography (PLC) on silica gel (Merck PF $_{254+366}$) into starting material (0.01 g), 4-bromobiphenyl (*2*, 0.11 g$\sim$22 %) and *p*-terphenyl (*3*, 0.24 g$\sim$48 %). The plate was developed twice with light petroleum, b.p. 50 – 70 °C. The *p*-terphenyl was identified by elemental analysis and by comparison of the IR spectrum with a published spectrum.[13]

Similarly, compound *2* (0.50 g) in benzene (1.50 l) was photolysed for 14 h. The residue was separated by PLC into starting material (0.14 g) and *p*-terphenyl (0.21 g$\sim$58 % of reacted starting material). The plate was developed twice with methylcyclohexane.

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