Kinetics of Reactions of Benzyl Chloride Cation Radical, Dichloride Anion, Dibromide Anion and Solvated Electron Transients of Photodissociation of Benzyl Chloride and Benzyl Bromide in Water and Methanol Solutions

JOCHEN LILIE[a] and JOUKO KOSKIKALLIO[b]

[a]Hahn-Meitner-Institut für Kernforschung GmbH, Bereich Strahlenchemie, 1 Berlin 39, F.R.G. and
[b]Physical Chemistry Laboratory, Helsinki University, Meritullinkatu 1 C, SF-00170 Helsinki 17, Finland.

Laser flash photolysis of benzyl chloride and benzyl bromide in water and in methanol at 25 °C was monitored by electric conductance and light absorption. In water, photoheterolysis leads to the formation of the benzyl carbocation and Cl^- with a quantum yield $\phi=0.9\pm0.1$, and the benzyl chloride radical cation and the hydrated electron with $\phi=0.015\pm0.005$. The benzyl carbocation reacts fast with water, $k_5>1\times10^8$ s^{-1}, forming benzyl alcohol. e^-_{aq} reacts with benzyl chloride to benzyl radical, $k_8=(6.4\pm1)\times10^9$ dm^3 mol^{-1} s^{-1}. Benzyl chloride radical cation reacts with water forming benzyl alcohol and chlorine atom, $k_9=(1.5\pm0.2)$ 10^7 s^{-1}. In methanol benzyl radicals, $\lambda_{max}=304$ and 315 nm, originating from photohomolysis are the main products, $\phi=0.6\pm0.1$. The chlorine and bromine atoms, formed by photolysis, react with methanol, $k_{10}>1\times10^8$ s^{-1} and $k_{12}=(7.1\pm1)\times10^6$ s^{-1} respectively.

The reaction products from the photolysis of benzyl chloride in water or alcohol indicate both heterolytic and homolytic carbon–chlorine bond dissociation[1-4] of excited benzyl chloride, BzCl*.

$$BzCl^* \rightarrow Bz^+ + Cl^- \qquad (1)$$

$$BzCl^* \rightarrow Bz^· + Cl^· \qquad (2)$$

Cristol and Bindel[4] proposed that the heterolytic dissociation 1 takes place from the triplet state of benzyl chloride and the homolytic dissociation 2 from a singlet state. We[1] have found that 33 % of benzyl chloride dissociates heterolytically by reaction 1 in methanol, and a value of about 97 % was obtained by extrapolation for water. It was not clear whether the heterolytic products came from the initial step 1 or from the consecutive reactions 2 and 3 which compete with reaction 4.

$$Bz^· + Cl^· \rightarrow Bz^+ + Cl^- \qquad (3)$$

$$Bz^· + Cl^· \rightarrow BzCl \qquad (4)$$
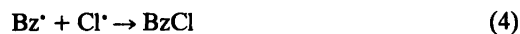
The reaction 4 cannot be important because the quantum yield of photodissociation of benzyl chloride[2] is close to 1. To get more direct information on the primary products and their relative yields and reaction rates a laser-photolysis study was performed. In addition to optical detection of intermediates, the conductivity was measured, which gives the necessary information on the charge of the primary products.

EXPERIMENTAL

Materials. Benzyl chloride, E. Merck Co, reagent grade, was distilled before use. Methanol and N_2O were used as received. Solutions containing 9.0×10^{-4} mol dm^{-3} benzyl chloride or benzyl bromide, 1.0×10^{-5} mol dm^{-3} HCl and 0.100 mol

dm^{-3} methanol were deaerated 10 min with argon gas and used immediately for flash experiments.

Photolysis. The Q-switched Neodym-YAG laser, System 2000, from JK-Laser Ltd. was used[5] in the flash photolysis experiments emitting 10 mJ frequency quadrupled light pulses at 265 nm of about 10 ns half-width.

In order to obtain quantum yields of the transients the intensity of the light pulse was calculated from the experimental linear dependence of the photocell reading with the change of conductivity of an aqueous $K_4Fe(CN)_6$ solution at pH 5 due to solvated electrons formed by the photolysis.[6] The light intensity was varied by a factor of about 10 by using filters. Less than 2 % of benzyl chloride was photodissociated by one unfiltered light pulse. The transients observed were all formed by a monophotonic process. This was demonstrated by a linear dependence of the transient concentration with the light intensity which was decreased by filters to about 0.2 times the maximum intensity and in the case of solvated electrons to about 0.11 times the maximum intensity. According to Lachish et al.[7] a linear correlation can be obtained also for biphotonic processes within limited range of light intensities but the line does not involve the origin of low intensities. In our experiments the straight line passes through the origin. Saturation effects are expected[7] if $\varepsilon \geq 3.5 \times 10^3$ for laser flash photolysis. For benzyl chloride at 265 nm ε is less than 0.1 times the value for saturation. This was verified by the linear intensity dependence.

Data from both light absorption and conductivity detection systems were digitized and processed on PDP 11/40 computer. Pseudo first order kinetics of the reactions of the transients were demonstrated by varying the transient concentration using light intensities which were varied by a factor of about 5. This also indicates that the reaction products such as benzyl alcohol did not change the yields or rates of transients. The standard deviation of the calculated rate constant obtained from the fit of first order rate law to the experimental values was about ±5 % or better in each case. The reproducibility of rate constants obtained in different experiments with different wavelengths of detection or different experimental conditions was about ±10 % or less, Table 1. The concentrations of H^+_{aq}, Cl and BzCl were corrected for the slow hydrolysis of benzyl chloride[8] in water at 25 °C, $k=1.48 \times 10^{-5}$ s^{-1}.

RESULTS AND DISCUSSION

Photodissociation of benzyl chloride in water. Benzyl chloride was excited by 10 ns laser flash light of 265 nm in water containing 0.100 mol dm^{-3} methanol and 9.0×10^{-4} mol dm^{-3} of benzyl chloride and about 1.0×10^{-5} mol dm^{-3} hydrochloric acid. The reaction products and transients were monitored by change in conductivity or by light absorption using different wavelengths between 310 nm and 650 nm. The photodissociation by reactions 1 and 2 was faster

Table 1. Half-lives of disappearance and formation of transients in the photolysis of benzyl chloride, monitored by changes in the electric conductivity and light absorbance in water containing 0.100 mol dm^{-3} methanol or in methanol, both with 1.0×10^{-5} mol dm^{-3} HCl, and 9.0×10^{-4} mol dm^{-3} BzCl at 25 °C.

Transient	Solvent	λ/nm	$t_{1/2}$/ns	Mean
BzCl$^{\cdot+}$	water	320	48.1	
BzCl$^{\cdot+}$	water	330	42.5^b	
BzCl$^{\cdot+}$	water	340	52.8^c	
BzCl$^{\cdot+}$	water	350	47.1^b	
BzCl$^{\cdot+}$	water	360	43.1,40.8^b,45.8^d	
BzCl$^{\cdot+}$	water	370	38.4^b	
BzCl$^{\cdot+}$	water	380	56.4^b	47±5
BzCl$^{\cdot+}$	water	360	30.2^a	
Cl$_2^-$	water	320	3000	
Br$_2^-$	water	350	326^e, 360^e 333^e	340±20
e$^-_{aq}$	water	600	104^c, 111^c, 114, 122, 130	113±10
Bz$^{\cdot}$	methanol	310	6100	

^{a} 1.30 10^{-4} mol dm^{-3} HCl, ^{b} saturated with N_2O, ^{c} no methanol, ^{d} 5 vol. per cent methanol, ^{e} half-life of increase.
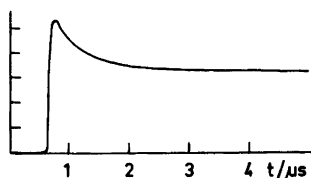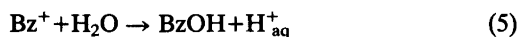
Fig. 1. Change of conductance after one flash in aqueous solution of benzyl chloride, expressed in arbitrary units, mainly due to the formation of H_{aq}^+, Cl^- and formation and disappearance of e_{aq}^-.
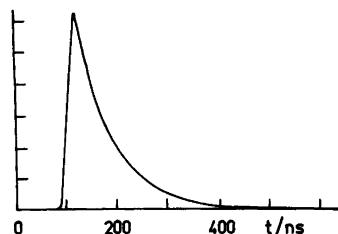

Fig. 2. Change of absorbance in arbitrary untis at 600 nm in flash photolysis of benzyl chloride, due to formation and disappearance of solvated electron in aqueous solution by reactions 7 and 8.

than the half-width of the flash light, about 10 ns, and the rates could not be measured. The change in conductivity (Fig. 1) shows that the ions H_{aq}^+ and Cl^- are formed in less than 10 ns. The quantum yield of benzyl chloride photodissociation calculated from the change of conductance is about 0.9 ± 0.1. Kuzmin *et al.*[2] obtained a value of 1.0 for the quantum yield of photodissociation of benzyl chloride in 1:1 methanol–water solution and Ichimura *et al.*[9] obtained a value of 0.9 in gas phase. A value of 0.35 was found in *tert*-butyl alcohol by Cristol and Bindel.[4] Weak fluorescence, $\phi_F=1\times10^{-4}$, and phosphorescence $\phi_p=1\times10^{-2}$ was obtained by Ichimura *et al.*[9] for benzyl chloride in a hydrocarbon solid matrix at 77 K in agreement with the dominant photodissociation, the photodissociation half-life in the gas phase obtained by Ichimura *et al.*[9,10] is about $t_{1/2}=0.07$ ns, the fluorescence half-life $t_F=10-40$ ns and the quantum yield $\phi_F=4.5\times10^{-4}$.

The reaction products[1-4] indicate that benzyl carbocation Bz^+ is formed together with Cl^- during the photolysis of benzyl chloride [eqn. (1)]. Bz^+ reacts in less than 10 ns with water forming benzyl alcohol and H_{aq}^+ [eqn. (5)] as indicated by our conductivity experiments.

$$Bz^+ + H_2O \rightarrow BzOH + H_{aq}^+ \qquad (5)$$

Both reactions 1 and 5 were too fast to be measured and a lower limit for the rate constant of reaction 5 was obtained, $k_5 > 1\times10^8$ s^{-1} at 25 °C in water. Jones and Dorfman[11,12] have measured the second-order rate constant $k_5=1.8\times10^7$ dm^3 mol^{-1} s^{-1} in dichloroethane, which corresponds to a first-order rate constant $k_5=1\times10^9$ s^{-1} in water, when solvent effects are neglected.

Solvated electron. Solvated electrons were formed by a monophotonic mechanism in laser flash photolysis of benzyl chloride in water [eqn. (6)].

$$BzCl + h\nu \rightarrow BzCl^{\cdot+} + e_{aq}^- \qquad (6)$$
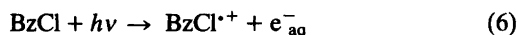
The disappearance of solvated electrons was monitored by the absorbance at $\lambda=600$ nm (Fig. 2), and by the decrease in electric conductivity after the fast initial rise (Fig. 1). When water was saturated with N_2O no transients could be detected by conductivity measurements or by absorbance at 600 nm, because of the rapid reaction[13] of N_2O with solvated electrons $(k=8.7\times10^9$ dm^3 mol^{-1} s$^{-1})$. Likewise in water containing 1.3×10^{-4} mol dm^{-3} HCl no transients could be observed by conductivity measurements, owing to the rapid reaction[13] of H_{aq}^+ with solvated electrons, $k=2.3\times10^{10}$ mol dm^{-1} s^{-1}.

The quantum yield of solvated electron, reaction 6, $\phi=0.015\pm0.005$, was calculated using the observed value $\phi\varepsilon=200$ dm^3 mol^{-1} cm^{-1} and the reported[14] value of $\varepsilon=12\,000$ dm^3 cm^{-1} at 600 nm. Solvated electrons are formed[15] by photolysis of aromatic compounds in water from the first excited singlet state S_1, and the quantum yield is 0.017 for phenol at 30 °C. The CH_2Cl group is a weak electron acceptor with a substitution constant[15] of $\sigma_m=0.17$ and $\sigma_p=0.17$ which are not much different from the respective values for OH group, $\sigma_m=0.32$ and $\sigma_p=0.37$.

The first-order disappearance of the solvated electrons, monitored by absorption at $\lambda=600$ nm, was independent of the flash light intensity altered by a factor of nine. The change of conductivity was somewhat slower and may involve other reactions in addition to reactions 7

and 8. In water containing 0.10 mol dm^{-3} methanol and 3.0×10^{-5} mol dm^{-3} HCl, and about 9.0×10^{-4} mol dm^{-3} BzCl, solvated electrons react with both H_{aq}^+ and benzyl chloride.

$$e_{aq}^- + H_{aq}^+ \rightarrow H^\cdot + H_2O \qquad (7)$$

$$e_{aq}^- + BzCl \rightarrow Bz^\cdot + Cl^- \qquad (8)$$
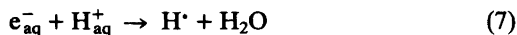
Using the value $k_7=2.3\times10^{10}$ mol dm^{-3} s^{-1}, a value of $k_8=(6.4\pm1)$ 10^9 dm^3 mol^{-1} s^{-1} is obtained. This value can be compared with the value $k_8=(4.5\pm0.5)$ 10^9 dm^3 mol^{-1} s^{-1}, reported by Lichtscheidl and Getoff.[13]

Benzyl chloride cation radical. A transient was observed in the flash photolysis of benzyl chloride in water at $\lambda_{max}=330$ nm, $\phi\varepsilon=400$ dm^3 mol^{-1} cm^{-1}. The formation of the transient is fast and the rate could not be measured (half-life $t_{1/2}<10$ ns). the first-order decay rate was measured from the change in absorbance at different wavelengths from 320 nm to 380 nm (Table 1). The absorption of this transient is different from the absorptions reported by Treinin *et al.*[17] and by Jayson *et al.*[18], $\lambda_{max}=320$ nm for Cl$^\cdot$ and $\lambda_{max}=340$ for Cl$_2^-$. We assign the observed transient absorption to benzyl chloride radical cation formed together with e$_{aq}^-$ from benzyl chloride (eqn. 6). The benzyl chloride radical cation reacts with water by reaction 9.

$$BzCl^{\cdot+} + H_2O \rightarrow BzOH + H_{aq}^+ + Cl^\cdot \qquad (9)$$
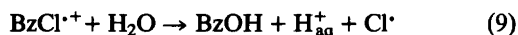
The rate constant $k_9=(1.5\pm0.2)\times10^7$ s^{-1} is of the order of magnitude expected[19] for the reaction. The absorption spectrum of the benzyl chloride radical cation is not known, but $\lambda_{max}\approx400$ nm is reported by Shida and Hamill[20] for the toluene cation radical in the solid matrix.

Chlorine atom and benzyl radical. Chlorine atoms and benzyl radicals, formed by reactions 2, 8 and 9, comprise about 3 % of the products of benzyl chloride photolysis.[1] In water containing 0.10 mol dm^{-3} methanol and about 3.0×10^{-5} mol dm^{-3} Cl$^-$ ion the following reactions are expected to occur.

$$Cl^\cdot + CH_3OH \rightarrow {}^\cdot CH_2OH + H^+ + Cl^- \qquad (10)$$

$$Cl^\cdot + Cl^- \rightarrow Cl_2^- \qquad (11)$$

A slowly decaying transient was observed after the benzyl chloride radical cation had dis-
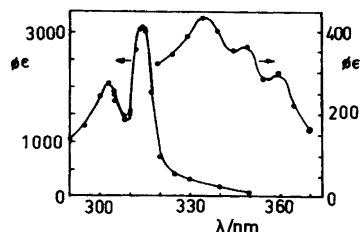

Fig. 3. Transient spectra of benzyl radical obtained by laser flash photolysis of benzyl chloride in methanol (left) and transient spectra of Cl$_2^-$ obtained in water (right). Unit of $\phi\varepsilon$ is dm^3 mol^{-1} cm^{-1}.

appeared, $\lambda_{max}=(335\pm5)$ nm (Fig. 3). This value is close to the $\lambda_{max}=340$ nm reported[17,18] for the Cl$^{\cdot-}$. Due to reactions 6 and 9 the quantum yield of chlorine atoms is equal to the quantum yield of benzyl cation radicals and equal to that of solvated electrons, $\phi=0.015$. The quantum yield of chlorine atoms formed by photolysis of benzyl chloride $\phi\approx0.03\pm0.01$ was obtained by extrapolation from previous results.[1] Using the experimental value of $\phi\varepsilon=(400\pm100)$ dm^3 mol^{-1} cm^{-1} we calculated a value of $\varepsilon=(13000\pm4000)$ dm^3 mol^{-1} cm^{-1} for Cl$_2^-$ at 340 nm. This is fairly close to the reported[17,18] value $\varepsilon=8800$ dm^3 mol^{-1} cm^{-1} for Cl$_2^-$.

In the gas phase, chlorine atoms react rapidly with methanol,[21] $k_{10}=3.4\times10^{10}$ dm^3 mol^{-1} s^{-1}. In water chlorine atoms are converted[16,17] into the less reactive ions ClOH$^{\cdot-}$ and Cl$_2^-$. The measured half-life for the first-order disappearance of the transients ClOH$^{\cdot-}$ and Cl$_2^-$ is $t_{1/2}=(3\pm1)\times10^{-6}$ s.

The photolysis of benzyl chloride produces[1–4] benzyl radicals by reactions 2 and 8. We observed a transient for which the absorption spectra, Fig. 3, was identical with the spectra of benzyl radical obtained by Christensen *et al.*[22] and by Mittal *et al.*[23] in water. We obtained a value of $\phi\varepsilon=(200\pm50)$ dm^3 mol^{-1} cm^{-1} for benzyl radical formed in the flash experiment at 320 nm. For the molar absorption of benzyl radical a value of $\varepsilon=5.5\times10^3$ dm^3 mol^{-1} at $\lambda=318$ nm has been reported.[21,22] Using these values a quantum yield of $\phi=0.036\pm0.01$ is obtained for the benzyl radical, which is close to the value 0.03 ± 0.01 calculated from previous results.[1] The value of quantum yield 0.015 obtained for solvated electron formed by reaction 6 can be compared with

the quantum yield of benzyl radical 0.036 formed by reactions 2 and 8 and the quantum yield of radical products calculated from the previous results[1] 0.03. These values show that benzyl radicals and chlorine atoms are formed in the photolysis of benzyl chloride due to reactions 2 and 8 to approximately equal amounts.

Photolysis of benzyl chloride and benzyl bromide in methanol. A transient was detected during the photolysis of benzyl chloride and benzyl bromide in methanol which had absorption maxima at 304 nm and 315 nm (Fig. 3) and $\phi\varepsilon_{304}$=2200 dm^3 mol^{-1} cm^{-1} and $\phi\varepsilon_{315}$=3500 dm^3 mol^{-1} cm^{-1}, respectively. This transient absorption is identical to that reported previously[21,22] for the benzyl radical. Using the values ε_{307}=3300 dm^3 mol^{-1} cm^{-1} and ε_{318}=5500 dm^3 mol^{-1} cm^{-1} reported[13,22,23] for the benzyl radical in water ϕ=0.6±0.1 is obtained, which is close to the quantum yield ϕ=0.67 calculated for reaction 2 from the values of the amounts of products of photolysis of benzyl chloride in methanol obtained previously.[1] No absorption due to chlorine atoms or Cl_2^- were observed in methanol, in contrast to the photolysis experiments in water, although relatively large amounts of chlorine atoms were formed by reaction 2. This result can be explained by assuming a fast reaction 10.

An immediate increase of the conductivity, $\Delta\lambda$=120 Ω^{-1} cm^2, was observed in the flash photolysis of benzyl chloride. For benzyl bromide we obtained an immediate increase, $\Delta\lambda$=40 Ω^{-1} cm^2, followed by a slower first-order increase of $\Delta\lambda$=70 Ω^{-1} cm^2. For this reaction the calculated rate constant is k_{12}=(7.1±1)×10^6 s^{-1}, and it is attributed to the reaction 12 of bromine atoms with methanol.

$$Br^\bullet + CH_3OH \rightarrow {}^\bullet CH_2OH + H^+ + Br^- \quad (12)$$
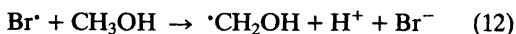
The corresponding reaction for Cl$^\bullet$ [eqn. (10)] was too fast to be detected and therefore only one step was observed for the change of conductivity. The fast initial step in the photolysis of benzyl bromide is due to heterolytic dissociation 13, followed by a fast reaction of benzyl carbocation with methanol.
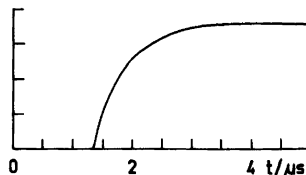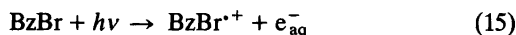
$$BzBr + h\nu \rightarrow Bz^+ + Br^- \quad (13)$$

$$Bz^+ + CH_3OH \rightarrow BzOCH_3 + H^+ \quad (14)$$

Fig. 4. Change of absorbance in arbitrary units at 350 nm in flash photolysis of benzyl bromide in aqueous solution, due to formation of Br$_2^-$ by reaction 17.

Photolysis of benzyl bromide in water. The quantum yield ϕ=0.9±0.1 was obtained by conductivity measurements for the heterolytic photodissociation 13 of benzyl bromide in water. The quantum yield ϕ=0.015±0.05 for the formation of solvated electrons calculated from the absorbance at 600 nm is equal to the corresponding value obtained from photolysis of benzyl chloride. The rate constant of the reaction of solvated electrons with benzyl bromide, k=(4.0±0.5)×10^6 s^{-1} is equal within experimental error, to the value obtained for reaction 8 in the photolysis of benzyl chloride.

A transient absorption was observed at λ_{max}=350 nm after the flash photolysis of benzyl bromide (Fig. 4). This absorption agrees with the reported[17,18] value λ_{max}=360 nm for Br$_2^-$. It is formed by the reactions 15−17.

$$BzBr + h\nu \rightarrow BzBr^{\bullet+} + e_{aq}^- \quad (15)$$

$$BzBr^{\bullet+} + H_2O \rightarrow BzOH + H_{aq}^+ + Br^\bullet \quad (16)$$

$$Br^\bullet + Br^- \rightleftarrows Br_2^- \quad (17)$$

For the transient Br$_2^-$ we observed a value of $\phi\varepsilon$=(650±50) dm^3 mol^{-1} cm^{-1}. In addition to reaction 16 unknown amounts of bromine atoms are expected to be formed in homolytic photodissociation of benzyl bromide. Therefore the quantum yield of Br$^\bullet$ is not known and the molar absorption ε of Br$_2^-$ cannot be calculated.[17,18]

The rate constant of reaction 17, k_{17}=(1.2±0.2)×10^{10} dm^3 mol^{-1} s^{-1}, was calculated from the rate of increase of the 360 nm absorption at different Br$^-$ concentrations. This value is in agreement with k_{17}=1.1×10^{10} dm^3 mol^{-1} s^{-1} reported previously.[17,18] The transient Br$_2^-$ disappears by first-order reaction and the rate constant is k=(3.5±1)×10^4 s^{-1}.

No transient absorption due to the benzyl bromide cation radical was observed due to a fast reaction 16 of the cation radical.

CONCLUSIONS

The rapid appearance of ionic products, and the relatively slow reaction between Br· and methanol, indicate that, in aqueous solution, the main reaction of benzyl chloride and benzyl bromide, excited at $\lambda=265$ nm, is heterolytic dissociation. About 90 per cent of the excited benzyl chloride or benzyl bromide molecules react to form benzyl carbocations Bz$^+$, which react in less than 10 ns with water to form benzyl alcohol. About 2 % of excited benzyl chloride produces benzyl chloride radical cations and an equivalent amount of hydrated electrons. Benzyl chloride radical cation reacts with water in a second step producing chlorine atoms. Solvated electron reacts with benzyl chloride to yield the benzyl radical. These primary products indicate that the products attributed previously[1] to homolytic dissociation originate partly from a reaction producing solvated electrons. The possibility, considered previously[1], that Bz$^+$ is formed in the consecutive reactions 1 and 3 can be ruled out as the major process.

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