

Lifetimes of **a**-halo and **a**-azidobenzyl carbocations in aqueous solution

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Abstract. The title cations were produced in aqueous solution by chemical initiation (solvolysis) of benzyl-*gem*-dihalides and benzyl-*gem*-diazides. The solvolysis reactions of benzyl-*gem*-dihalides and benzyl-*gem*-diazides in water proceed by a stepwise mechanism through **a**-halobenzyl carbocation and **a**-azidobenzyl carbocation intermediates, which are captured by water to give the corresponding carbonyl compounds as the sole detectable products. Rate constant ratio k_x/k_s (M^{-1}) for partitioning of the carbocation between reaction with halide/azide ion and reaction with water is determined by analysis of halide/azide common ion inhibition of the solvolysis reaction. The rate constants k_s (s^{-1}) for the reaction of the cation with solvent water were determined from the experimental values of k_x/k_s and k_{xw} for the solvolysis of the benzyl-*gem*-dihalides and benzyl-*gem*-diazides respectively, using $k_x = 5 \times 10^9 M^{-1} s^{-1}$ for diffusion-limited reaction of halide/azide ion with **a**-substituted benzyl carbocations. The values of $1/k_s$ are thus the lifetimes of the **a**-halobenzyl carbocations and **a**-azidobenzyl carbocations respectively.

Keywords. Solvolysis; lifetimes; **a**-halobenzyl carbocations; **a**-azidobenzyl carbocations.

1. Introduction

Substitution reactions of benzyl derivatives have been studied for most of this century^{1–3}, and these investigations have been several to the development of the theory of nucleophilic substitution at saturated carbon^{1–10}. In the study of solvolysis reactions of some benzylchlorides, benzalchlorides and polychloromethyl ethers it was concluded that these reactions proceed through stable carbocation intermediates. This was attributed to the contributions of additional structures in which a positive charge is developed on **a** chlorine¹¹ and in the case of **a**azidobenzyl carbocations on the azido group. Also there were few reports of salt and deuterium isotope effects on solvolytic reactions of benzalchlorides in aquo-organic mixed solvents^{12–14}. In the present study, we wish to report the lifetimes of **a**halobenzyl carbocations and **a**azidobenzyl carbocations in water not reported so far, in order to explore their reactivity with several nucleophiles such as carbanionic nucleophiles and nitrogen nucleophiles or oxygen nucleophiles so that it will be possible to build a new carbon–carbon, carbon–nitrogen and carbon–oxygen bond respectively, resulting in the synthesis of new simple organic molecules.

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2. Experimental

Solvolysis rate constants for the reaction of the benzyl-*gem*-dihalides and benzyl-*gem*-diazides were determined in water containing 1% acetonitrile at 25°C and at constant ionic strength of 1.0 M, maintained with NaClO₄. Solvolysis reactions of benzyl-*gem*-dihalides and benzyl-*gem*-diazides were initiated by 100-fold dilution of a solution of substrate in acetonitrile into the reaction mixture to give a final concentration of 1.0×10^{-4} M (injecting 30 μ L of the stock solution of the substrate in acetonitrile into 3 mL of water containing 1 M NaClO₄ in the quartz cell of 1 cm path length). First, the time-dependent UV-Visible absorption spectrum of the solvolysis reaction was recorded. This spectrum gives the I_{\max} of the reactant and that of the product as well. As a typical example, the time dependent UV-Visible absorption spectrum of the solvolysis reaction of benzyl-*gem*-dichloride is given in figure 1. Such absorption spectra were first recorded for all the benzyl-*gem*-dihalides and benzyl-*gem*-diazides. Thus by knowing I_{\max} of all the ring-substituted benzaldehyde/acetophenone products from the time-dependent UV-Visible absorption spectrum, the kinetic experiments were followed spectrophotometrically by monitoring the appearance of corresponding benzaldehydes/acetophenones at their I_{\max} . The values of I_{\max} for various ring-substituted benzaldehydes/acetophenones are given in table 1. Also for verification purpose, monitoring the disappearance of benzyl-*gem*-dichloride at its I_{\max} followed the reaction. All spectrophotometric experiments were performed on UVIKON 923 UV-Vis spectrophotometer, which was supplied with necessary software for performing the experiments, storing and analysing the experimental data. KaleidaGraph supplied by Synergy Software, USA, and carried out the analysis of the data. Conductivity and pH metric experiments were carried out on a conductivity bridge and pH meter respectively,

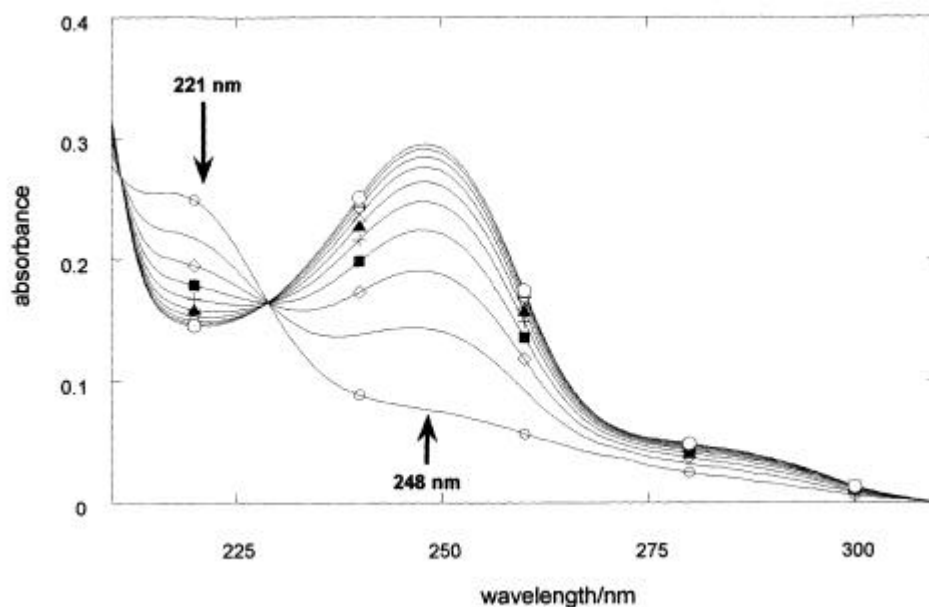


Figure 1. Time-dependent UV-Vis spectrum of benzyl-*gem*-dichloride in water at 25°C.

Table 1. I_{\max} values for various benzaldehydes/acetophenones.

Benzaldehyde/acetophenone	I_{\max}	Benzaldehyde/acetophenone	I_{\max}
Benzaldehyde	248	Acetophenone	249
4-Fluorobenzaldehyde	250	4-Fluoroacetophenone	251
4-Methoxy benzaldehyde	294	4-Methoxy acetophenone	310
4-Methyl benzaldehyde	259	4-Methyl acetophenone	265
4-Chloro bezaldehyde	259	4-Chloro acetophenone	259
4-Nitro benzaldehyde	263	4-Methoxy propiophenone	297
3-Fluorobenzaldehyde	245	4-Methoxy benzophenone	305

supplied by Digisun Electronics Systems, Hyderabad. Again the rate constants by these methods were evaluated using the KaleidaGraph software. Running the UV-Vis spectrum of the authentic aldehydes/acetophenones identified the products as the corresponding benzaldehydes/acetophenones.

3 Results and discussion

The solvolysis reactions of benzyl-*gem*-dihalides and benzyl-*gem*-diazides in water at 25°C and $I=1.0\text{ M}$ (NaClO_4) gave the corresponding benzaldehydes as the sole detectable product (99%). Figure 1 shows the time-dependent UV-Vis absorption spectrum for the solvolysis of benzyl-*gem*-dichloride (cation 1, chart 1). With time at 221 nm there is decrease in the absorbance and at 248 nm there is increase in absorbance, thus the former at 221 nm refers to the depletion of the starting *gem*-dichloride and the later refers at 248 nm to the growth in the product benzaldehyde. After completion of the reaction the final spectrum was identical with that of the authentic benzaldehyde. First-order solvolysis rate constants for these reactions in the absence of chloride ion, k_{solv} , (s^{-1}), was determined by monitoring either the appearance of corresponding benzaldehyde or the disappearance of benzyl-*gem*-dichloride by UV spectroscopy (figure 2) or by monitoring the decrease in pH due to production of H^+ ions or by monitoring the increase in conductivity due to production of H^+ and Cl^- ions. It is observed that all the four sets of rate constants were found to be identical within 5% deviation. Figure 3 shows the dependence of the normalized rate constant ratio, $k_{\text{obsd}}/k_{\text{solv}}$, for benzyl-*gem*-dichloride on the concentration of added chloride ion, where k_{obsd} is the observed rate constant at a given concentration of chloride ion and k_{solv} is the rate constant in the absence of added chloride ion.

The chloride ion inhibition shows that the reactions of benzyl-*gem*-dichloride proceed by stepwise mechanism through the diffusionally equilibrated *achlorobenzyl* carbocation that can be trapped competitively by added chloride ion and solvent water (scheme 1). This kind of common ion inhibition on the solvolysis rates was observed for all the starting compounds studied. Figure 4 shows linear re-plot of the data from figure 3 according to (1), derived applying steady state approximation to the intermediate carbocation, for the mechanism shown in scheme 1.

$$\frac{k_{\text{solv}}}{k_{\text{obsd}}} = 1 + \left(\frac{k_{\text{Cl}}}{k_{\text{s}}} \right) [\text{Cl}^-]. \quad (1)$$

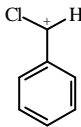
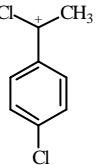
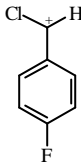
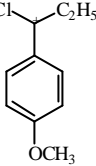
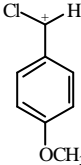
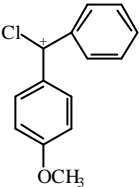
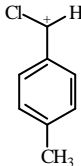
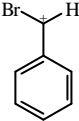
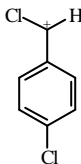
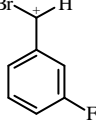
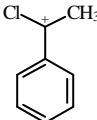
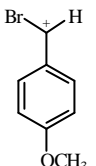
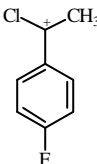
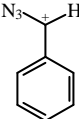
No.	Cation	Lifetime in ns	No.	Cation	Lifetime in ns
1		0.15	10		0.12
2		0.2	11		2.1
3		0.4	12		>2.1
4		0.33	13		0.2
5		0.1	14		< 0.2
6		0.5	15		20
7		0.16	16		17

Chart 1. (Continued)

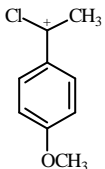
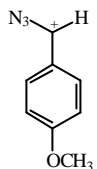
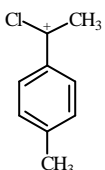
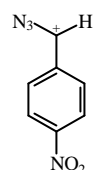
No.	Cation	Lifetime in ns	No.	Cation	Lifetime in ns
8		1.4	17		1700
9		0.36	18		1.2

Chart 1. *a*-Halo and *a*-azidobenzyl carbocations and their lifetimes in water at 25°C.

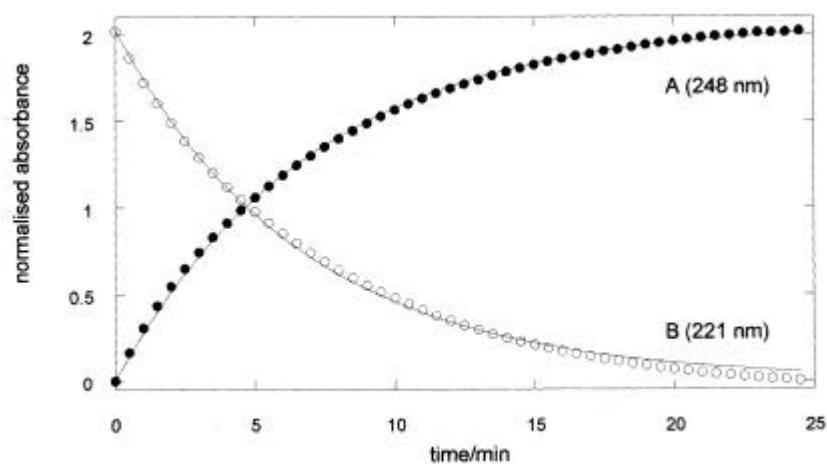


Figure 2. Curve A: Build up of benzaldehyde at 248 nm; Curve B: Decay of benzyl-*gem*-dichloride at 221 nm.

There was no detectable lag in the formation of corresponding benzaldehyde, which shows that there is no accumulation of the intermediate chloro/bromo/azidohydrins (X-1-OH, scheme 1), whose reactivities are therefore much greater than those of the parent benzyl-*gem*-dihalide/diazide (X-1-X). In no case was there any detectable formation of the ring-substituted N-(*a*-chloro)benzyl acetamide (scheme 2) by the reaction of cation with acetonitrile (Ritter reaction)¹⁵ (acetonitrile was used as solvent for making stock solutions of the substrates and each time 30 μ L of this solution was used for initiating the reaction. This gives approximately 0.19 M of acetonitrile in solution). This shows that the pseudo-first order rate constants for the reaction of the halo/azido benzyl carbocations with solvent water, k_s , are much larger than those for Ritter type

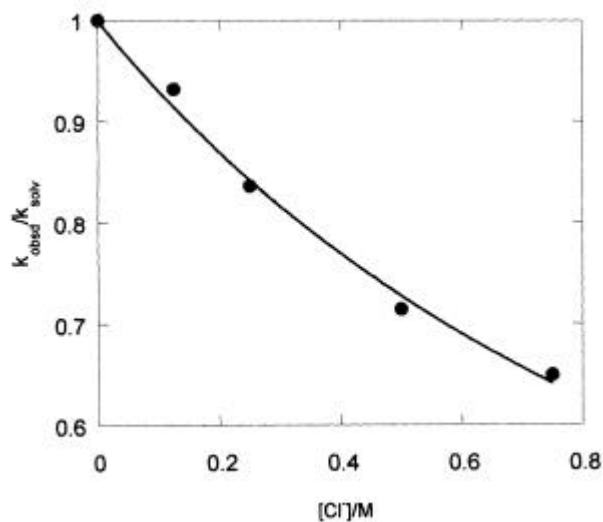


Figure 3. Effect of $[\text{Cl}^-]$ on k_{solv} for benzyl-*gem*-dichloride in water at 25°C, $I = 1.0 \text{ M}$ (NaClO_4).

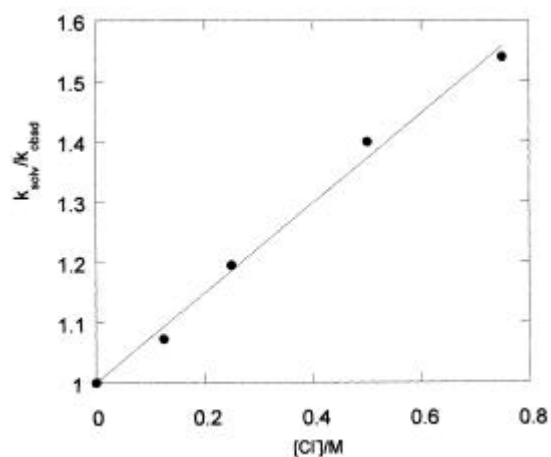
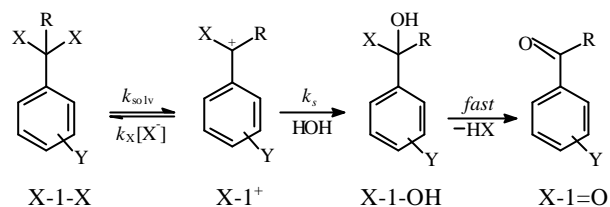


Figure 4. Normalized replot from the data of figure 3.

reaction. The common ion inhibition of the solvolysis of the benzyl-*gem*-dihalides and diazides by added chloride or bromide or azide ion (figures 3 and 4) provides classic evidence for a stepwise $\text{D}_\text{N} + \text{A}_\text{N}$ ($\text{S}_\text{N}1$)^{16,17} mechanism, with rate determining cleavage of benzyl-*gem*-dihalides/diazides to form diffusionally-equilibrated carbocation reaction intermediates which can be trapped by halide/azide ion and by solvent. The capture of *a* halo/azido benzyl carbocations by added halide/azide ion leads to a reduction in their steady-state concentration and hence in k_{obsd} for solvolysis of the starting benzyl-*gem*-dihalides/azides. The good fit to (1), derived for the mechanism, shown in scheme 1, of the kinetic data for solvolysis of benzyl-*gem*-dihalides/azides in the presence of



(Note: The final products are benzaldehyde if $R = H$ and two moles of HCl or HBr or HN_3 if $X = \text{Cl}$ or Br or N_3 and acetophenone if $R = \text{CH}_3$; Y is always a para substituent except in **14**)

$R = H$; $X = \text{Cl}$: (1) $Y = H$, (2) $Y = F$, (3) $Y = \text{OCH}_3$, (4) $Y = \text{CH}_3$, (5) $Y = \text{Cl}$

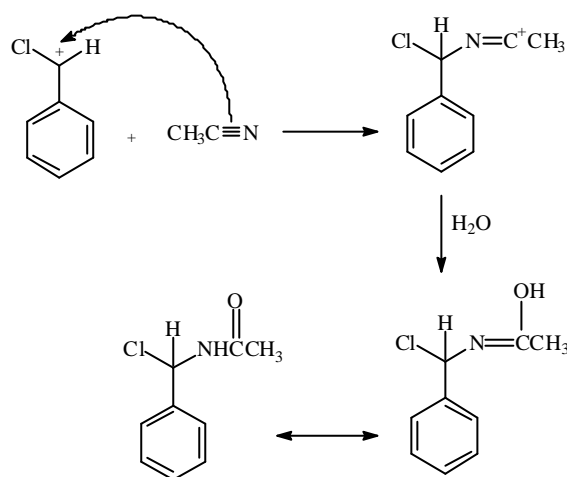
$R = \text{CH}_3$; $X = \text{Cl}$: (6) $Y = H$, (7) $Y = F$, (8) $Y = \text{OCH}_3$, (9) $Y = \text{CH}_3$, (10) $Y = \text{Cl}$

$Y = \text{OCH}_3$; $X = \text{Cl}$: (11) $R = \text{C}_2\text{H}_5$, (12) $R = \text{C}_6\text{H}_5$

$R = H$; $X = \text{Br}$: (13) $Y = H$, (14) $Y = 3\text{-F}$, (15) $Y = \text{OCH}_3$

$R = H$; $X = \text{N}_3^-$: (16) $Y = H$, (17) $Y = \text{OCH}_3$, (18) $Y = \text{NO}_2$

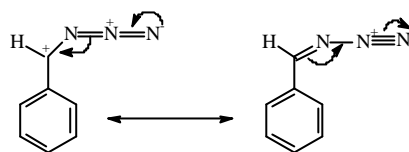
Scheme 1.



N-(α -chloro)benzyl acetamide

Scheme 2. Ritter reaction.

increasing concentration of halide/azide ion shows that the reactions proceed through liberated carbocation intermediates. For example, from the plot of $k_{\text{solv}}/k_{\text{obsd}}$ versus $[\text{Cl}^-]$ the value of k_{Cl}/k_s was obtained for benzyl-*gem*-dichloride (figure 4). Therefore, absolute rate constants $k_s(\text{s}^{-1})$ for capture of α -halo/azido benzyl carbocations by water were obtained from the rate constant ratios $k_x/k_s(\text{M}^{-1})$ for partitioning of the cations and using an estimated value for k_x ($5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) for the reaction of cation with X^- . Hence the lifetimes of these carbocations were obtained from the reciprocal of the k_s values and are given in chart 1.



Scheme 3.

Comparison of stabilities of **a**azidobenzyl carbocations with the rest of the carbocations

On comparing the lifetimes (chart 1) of the corresponding α -azidobenzyl carbo-cations⁵ with the rest of the **a**halobenzyl carbocations, it is observed that the **a**halobenzyl carbocations are more reactive towards water than the corresponding **a**azidobenzyl carbocations with the exception of the **a**azido-4-nitrobenzyl carbocation. This is attributed to the fact that the azido group is more effective at stabilizing the positive charge on the adjacent carbon by strong resonance effect (scheme 3)⁴.

The high reactivity of **a**azido-4-nitrobenzyl carbocation with water is again due to the presence of strong electron-withdrawing nitro substituent at para position, which overcomes the strong resonance effect of the azido group with cationic centre.

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