Carbocation lifetimes and entropy of water addition to carbocations dependent on their stability

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Abstract. Iminodiazonium ions (**a**-azidobenzyl carbocations) were produced in aqueous solution by chemical initiation (solvolysis) of benzyl-*gem*-diazides. Solvolysis reactions of benzyl-*gem*-diazides in water proceed by a stepwise mechanism through **a**-azidobenzyl carbocation intermediates, which are captured by water to give the corresponding carbonyl compounds as the sole detectable products. Rate constant ratio k_{az}/k_s (M^{-1}) for partitioning of the carbocation between reaction with azide ion and reaction with water was determined by analysis of azide common ion inhibition of the solvolysis reaction. Rate constants k_s (s^{-1}) for the reaction of the cation with solvent water were determined from the experimental values of k_{az}/k_s and k_{solv}, for the solvolysis of the benzyl-*gem*-diazides, using $k_{az} = 5 \times 10^9 \, M^{-1} \, s^{-1}$ for diffusion-limited reactions of azide ion with **a**-azidobenzyl carbocations. Values of $1/k_s$ were thus the lifetimes of the **a**-azidobenzyl carbocations. From the study of effect of temperature on k_{solv} and k_s the activation parameters are determined and discussed.

Keywords. Nucleophilic solvation; carbocation lifetimes; entropy of water addition; **a**-azidobenzyl carbocations.

1. Introduction

The iminodiazonium ions (**a**-azidobenzyl carbocations) are known to be the putative intermediates in organic chemistry.[1] As an example the Schmidt reaction of aldehydes and ketones in strongly acidic medium in presence of hydrazoic acid is a versatile approach to amides, lactams and nitriles.[1–4] The most widely accepted mechanism involves rearrangement with loss of molecular nitrogen from the putative imino-diazonium ions stabilized by an **a**-azido group to give the final products (scheme 1).[2,5,6]

It was also shown that the ring-substituted benzylic iminodiazonium ions (**a**-azido-benzyl carbocations) are generated in aqueous solution[7] and in dry acetonitrile (in presence of H^+)[8] as intermediates in the solvolyses of the corresponding *gem*-diazides which give chiefly the benzaldehydes[7] and Schmidt type products,[8] i.e. benzonitrile and formanilide respectively and small amount of benzaldehyde which is formed by the reaction of the cation with residual water present in the acetonitrile respectively. In the Schmidt type reaction[8] the amount of benzaldehyde formed increases with increase in amount of water added at the expense of the Schmidt type products. The ratio of the benzaldehyde to Schmidt-type products showed very strong mixed second- and third-order dependence on [water] as shown in the following equation.[8]
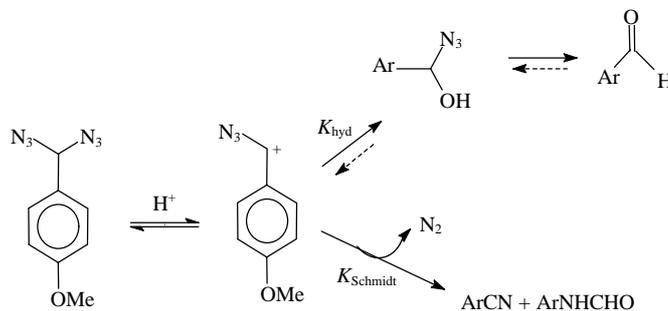
Scheme 1.
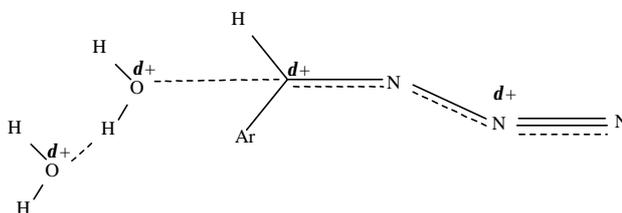
Scheme 2.

$$\frac{[\text{ArCHO}]}{[\text{Schmidt}]} = \frac{k_B([\text{H}_2\text{O}]_{\text{res}} + [\text{H}_2\text{O}]_{\text{add}}) + k_T([\text{H}_2\text{O}]_{\text{res}} + [\text{H}_2\text{O}]_{\text{add}})^2}{k_{\text{Schmidt}}}. \tag{1}$$

The ratio $k_T/k_B \approx 100\ \text{M}^{-1}$ shows that, in the relatively non-polar solvent acetonitrile, where formation of localized charge is unfavourable, the presence of a second water molecule in the transition state (scheme 2) for addition of water to the highly delocalised α-azidobenzyl carbocations provides substantial stabilization of the developing localized positive charge at the oxygen of the attacking water molecule. This was termed classical general base catalysis. But in spite of a good amount of extensive work on *a*-azidobenzyl carbocations in aqueous solution[7] except the determination of rate constants (k_s s^{-1}) for addition of water to *a*-azidobenzyl carbocations and kinetic barriers, the nature of the transition state for addition of water to the cations is not monitored and discussed. In view of the above observations and the 10 to 10^4 orders of magnitude lower reactivity of *a*-azidobenzyl carbocations towards water when compared to the diffusion limit ($5 \times 10^9\ \text{M}^{-1}\ \text{s}^{-1}$), it is planned in the present study to throw some light on activation parameters on solvolyses of the *gem*-diazides, k_{solv}, and on the nature of activation limited addition of water, k_s (now termed as nucleophilic solvation[9]) to *a*-azidobenzyl carbocations in aqueous solution.

2. Experimental

Solvolysis rate constants for the reaction of the benzyl-*gem*-diazides were determined in water containing 1% acetonitrile at 25°C and at a constant ionic strength of 2·0 M,

maintained with NaClO$_4$. The solvolysis reactions of benzyl-*gem*-diazides were initiated by making a 100-fold dilution of a solution of substrate in acetonitrile in to the reaction mixture to give a final concentration of $1 \cdot 0 \times 10^{-4}$ M (injecting 30 **ml** of the stock solution of the substrate in acetonitrile in to 3 ml of water containing 2 M NaClO$_4$ in the quartz cell of 1 cm path length). The kinetic experiments were followed spectrophotometrically by monitoring the appearance of corresponding benzaldehydes at their l_{max}. All spectro-photometric 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 carries out the analysis of the data. Running the UV-Vis spectrum of the authentic benzaldehydes identified the products as corresponding benzaldehydes.

3. Results and discussion

In the present work I have attempted to understand the effect of electron-donating and -withdrawing substituents on the thermodynamic stability and kinetic reactivity of *a*-azidobenzyl carbocations in aqueous solution. For this purpose three *gem*-diazides were selected, one with a highly electron-donating substituent, i.e. 4-MeO, the other with a highly electron-withdrawing substituent, i.e. 4-NO$_2$, and an unsubstituted *gem*-diazide. Solvolysis rate constants for the reaction of the 4-methoxybenzyl-*gem*-diazide (MBGDaz), benzyl-*gem*-diazide (BGDaz) and 4-nitrobenzyl-*gem*-diazide (NBGDaz) were spectrophotometrically determined in water by monitoring the appearance of the corresponding benzaldehydes at 275, 248 and 263 nm respectively.

In the absence of added azide ion, the reaction of MBGDaz did not exhibit clean first-order kinetics. This deviation was ascribed to the onset of common ion inhibition with accumulation of the azide ion leaving group. Rate constants for the this substrate in the absence of azide ion were therefore determined in the presence of 1 mM HClO$_4$, which served to protonate the accumulating azide ion leaving group and render it unreactive. There is no significant specific acid catalysis of the cleavage of this substrate by 1 mM HClO$_4$, because identical rate constants are observed for the reaction in the presence of HClO$_4$ (1–4 mM).

Solvolysis reaction of MBGDaz, BGDaz and NBGDaz in water at 25°C and $I = 2 \cdot 0$ M (NaClO$_4$) gave the corresponding benzaldehydes as the sole detectable product (99%). After the completion of the reaction the final spectrum was identical with that of authentic benzaldehydes. Pseudo-first-order rate constants for these reactions in the absence of azide ion, k_{solv} (s^{-1}), are determined by monitoring the appearance of corresponding 4-methoxy benzaldehyde (275 nm) by UV spectroscopy and fitting the data to a first-order rate equation. There is decrease in the normalized rate constant ratio k_{obsd}/k_{solv}, for BGDaz with concentration of added azide ion, where k_{obsd} is the observed rate constant at a given concentration of azide ion and k_{solv} is the rate constant in the absence of azide ion. Azide ion inhibition shows that the reactions of MBGDaz, BGDaz and NBGDaz proceed by a stepwise mechanism through the diffusionally equilibrated *a*-azidobenzyl carbocations that can be trapped by azide ion and solvent water (scheme 3).

According to (2) derived for the mechanism shown in scheme 3, the plot of k_{az}/k_s vs [N$_3^-$] was linear. The slopes of these plots of k_{az}/k_s (M^{-1}, scheme 3) are 8600 M^{-1} for MBGDaz, 86 M^{-1} for BGDaz and 6 M^{-1} for NBGDaz respectively, where k_{az} and k_s are the rate constants for the reaction of cation with azide ion and solvent water respectively.
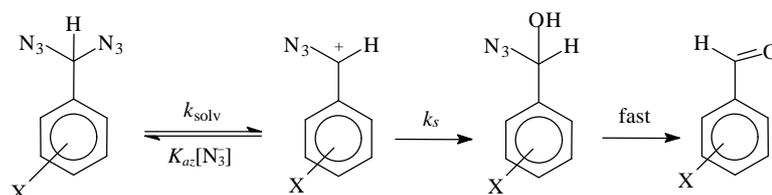
Scheme 3.

$$k_{\text{solv}} / k_{\text{obsd}} = 1 + (k_{az} / k_s)[\text{N}_3^-]. \tag{2}$$

The large reduction in the magnitude of azide common ion inhibition of the solvolysis of *gem*-diazido compounds as the *p*-substituent is changed from methoxy to nitro corresponds to a sharp decrease in the selectivity of the carbocation intermediates towards the azide ion, k_{az}/k_s (M^{-1}), with their increasing instability. Since the k_{az} (M^{-1}, s^{-1}) is limited by the rate of diffusional encounter of azide ion and *a*-azidobenzyl carbocations, which is independent of carbocation reactivity,[13–15] so that the entire change in the selectivity k_{az}/k_s is due to change in k_s for the activation-limited addition of water to *a*-azidobenzyl carbocations,[16,17] which prompted me to determine the activation parameters for the k_s process along with the k_{solv} process. A 10^6-fold larger value of k_{solv} for MBGDaz than that of NBGDaz (table 1) is obtained, which is consistent with a large development of positive charge at the benzylic carbon in the rate-determining transition state for solvolysis.

There was no detectable lag in the formation of corresponding benzaldehydes, which shows that there is no accumulation of the intermediate azidohydrins (scheme 3), whose reactivities are therefore much greater than those of the parent *gem*-diazides. In no case was there any detectable formation of the ring substituted N-alkyl amide by the reaction of cation with acetonitrile (Ritter reaction)[10] (acetonitrile was used as solvent for making stock solutions of the substrates and each time 30 *ml* 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 azidobenzyl cations with solvent water, k_s, are much larger than those for the Ritter type reaction. The common ion inhibition of the solvolysis of the gem-diazides by added azide ion provides classic evidence for a stepwise $D_N + A_N$ (S_N1)[11,12] mechanism, with rate-determining cleavage of *gem*-diazides to form diffusionally-equilibrated carbocation reaction intermediates which can be trapped by azide ion and by solvent. The capture of *a*-azidobenzyl cations by added azide ion leads to a reduction in their steady-state concentration and hence in k_{obsd} for solvolysis of the starting *gem*-diazides. The good fit to (2), derived for the mechanism shown in scheme 3, of the kinetic data for solvolysis of *gem*-diazides in the presence of increasing concentration of azide ion shows that the reaction proceeds through the liberated carbocation intermediates. From the plot of $k_{\text{solv}}/k_{\text{obsd}}$ versus $[\text{N}_3^-]$ the value of k_{az}/k_s was obtained. Therefore, absolute rate constants k_s (s^{-1}) for capture of *a*-azidobenzyl cations by water were obtained from the rate constant ratios k_{az}/k_s (M^{-1}) for partitioning of the cations and using the value, $k_{az} = 5 \times 10^9$ M^{-1} s^{-1} [13–15] in the reaction of cation with N_3^-. The k_s values at 25°C for *a*-azido-(4-methoxyphenyl)methyl cation, *a*-azidobenzyl cation and *a*-azido-(4-nitrophenyl)methyl cation are $5·8 \times 10^5$ s^{-1}, $5·8 \times 10^7$ s^{-1} and $8·6 \times 10^8$ s^{-1} respectively.

Hence the lifetimes of these cations were obtained from the reciprocal of the k_s values and are found to be 1.72×10^{-6} s, 1.72×10^{-8} s and 1.16×10^{-9} s, respectively. Hence these lifetimes are in accordance with carbocation stability, which means to say that, the **a**-azidobenzyl cation with a strongly electron-donating substituent like a MeO group at the para position is long lived ($k_s = 5.8 \times 10^5$ s^{-1}) than unsubstituted **a**-azidobenzyl cation in aqueous solution and readily formed ($k_{solv} = 0.62$ s^{-1}) in the solvolysis reaction. Whereas the same cation with a strong electron-withdrawing group like NO$_2$ at para position is shorter lived ($k_s = 8.6 \times 10^8$ s^{-1}) than unsubstituted **a**-azidobenzyl cation and more slowly formed ($k_{solv} = 4.9 \times 10^{-7}$ s^{-1}) in the solvolysis reaction. The lifetime and time for formation ($k_{solv} = 3.9 \times 10^{-4}$ s^{-1}) of unsubstituted **a**-azidobenzyl cation lies in between these two.

3.1 *Concerning activation parameters*

Activation parameters were determined from the respective experimental data using the Eyring equation.

$$k = (kT/h)\exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/RT). \tag{3}$$

Of particular importance are the negative sign and the magnitude of the $\Delta S^{\neq}_{solv}$ values (table 1). Values of -42 to -17 indicate extensive reorganization of the solvent shell in the transition state as a result of hydration of ions. In fact, during the solvolysis, as the leaving group departs it acquires a solvent shell which is increasingly bonded to it.[18] Hence freezing of solvent molecules takes place as the solvolysis proceeds, resulting in large negative entropies of activation for the solvolysis process. Among the three *gem*-azides, MBGDaz solvolysis has more negative entropy of activation than the solvolysis process of the other two *gem*-diazides. This can be explained as follows: Invoking the Hammond postulate,[19] one can assume that the geometry of the transition state resembles that of the intermediate carbocation (i.e. more towards the product) and that anything (here the electron-donating methoxy group) that increases the stability of the intermediate carbocation (due to direct resonance effect from the para position) will also lower the activation energy necessary to attain it. In fact the $\Delta H^{\neq}_{solv}$ for MBGDaz solvolysis is less than that of the other two *gem*-diazides (table 1). Therefore, from the less negative $\Delta S^{\neq}_{solv}$ value for NBGDaz solvolysis one can assume that the geometry of the transition state is less like that of the intermediate carbocation (i.e. is less product like) and again that anything (here the electron-withdrawing nitro group) that decreases the stability of the intermediate carbocation (again due to direct resonance effect from the para position) now increases the activation energy necessary to attain it. In fact, the $\Delta H^{\neq}_{solv}$ for NBGDaz solvolysis is more than that for the other two *gem*-diazides (table 1).

Regarding the activation parameters for the addition of water to the **a**-azidobenzyl cations, there is not much variation in the activation enthalpies, $\Delta H^{\neq}_s$ (table 1). However, the large differences in activation entropies, $\Delta S^{\neq}_s$ (table 1) do reflect on the nature of the intermediate cation and the transition state for the addition of water. Again, invoking the Hammond postulate, one can assume that the geometry of the transition state for the addition of water to 4-methoxy-**a**-azidobenzyl cation, which is less reactive towards water than the other two cations (cf k_s values) resembles more that of the intermediate carbocation (i.e. is more reactant like). Hence, more nucleophilic solvation of the cation

takes place, which causes more water molecules to be frozen. Therefore large negative entropy of activation is observed for addition of water to **a**-azido-4-methoxybenzyl cation. This was termed general base catalysis or stabilization by hydrogen bonding (scheme 2) without formal proton transfer.[8] From the lower negative entropy of activation (table 1), $\Delta S_s^{\neq}$ for addition of water to the more reactive cation, i.e. **a**-azido-4-nitrobenzyl cation, one can again assume that the geometry of the transition state for the addition of water to 4-nitro-**a**-azidobenzyl cation resembles the product more, presumably with formal proton transfer to the solvent.

In conclusion, the more stable cation i.e. less reactive **a**-azido-4-methoxybenzyl cation with reference to unsubstituted **a**-azidobenzyl cation, is formed in the solvolysis reaction (k_{solv}) and reacts with water (k_s), resulting in more negative entropies of activation, whereas the less stable cation i.e. **a**-azido-4-nitrobenzyl cation gives rise to less negative entropies of activation. The high enthalpies and modest entropies of activation for the solvolysis process are entirely in accordance with the progressive endothermic ionization of the benzyl-*gem*-diazides. Also the appreciably high negative entropy of activation for the addition of water to **a**-azido-4-methoxybenzyl cation and a very modest enthalpy of activation are in accordance with the developing covalent association of the carbocation with pressuably two to three water molecules by successive hydrogen bonding without any formal proton transfer (scheme 2). On the other hand, the very low negative entropy of activation for the addition of water to **a**-azido-4-nitrobenzyl cation reflects on its high reactivity (about 5 orders of magnitude less than the diffusional limit) with water. The unsubstituted azido benzyl cation lies in between these two. Similar arguments were made on entropy of activation very recently for even non-covalent association of water with 4,4′-dimethoxytrityl carbocation.[20]

Iso-kinetic temperatures were calculated for solvolysis (k_{solv}) and for the addition of water to **a**-azidobenzyl carbocations (k_s) according to the equation,[21]

$$\Delta H^{\neq} = \Delta H_0^{\neq} + b\Delta S^{\neq},$$

Table 1. Solvolysis of benzyl-*gem*-diazides in aqueous solution at 25°C and $I = 2.00$ (NaClO$_4$).

X	Temp. (°C)	k_{solv} (s^{-1})	k_s (s^{-1})	$\Delta H_{solv}^{\neq}$ (kJ/mol)	$\Delta S_{solv}^{\neq}$ (J/mol)	$\Delta H_s^{\neq}$ (kJ/mol)	$\Delta S_s^{\neq}$ (J/mol)
MeO	15	0·23	4.67×10^5				
	20	0·51	4.98×10^5				
	25	0·62	5.80×10^5	61·5	−41·7	14·4	−191
	30	0·93	6.54×10^5				
H	25	3.90×10^{-4}	5.80×10^7				
	30	7.02×10^{-4}	6.57×10^7				
	35	12.0×10^{-4}	7.39×10^7	85·5	−23·0	16·9	−40·0
	40	21.7×10^{-4}	8.42×10^7				
NO$_2$	25	0.490×10^{-6}	8.33×10^8				
	30	1.12×10^{-6}	9.81×10^8				
	35	1.95×10^{-6}	0.115×10^8	104	−17·2	18·3	−12·6
	40	4.01×10^{-6}	0.125×10^8				

by plotting enthalpies versus entropies. The b_{solv} value, i.e. the iso-kinetic temperature, for the solvolysis process is 1624 K which is well above the temperatures at which the reactions were carried out. Thus one can say that the solvolysis is essentially enthalpy controlled, whereas the b_s value, the iso-kinetic temperature, for the addition of water to *a*-azido benzyl carbocations is only 20 K, which is well below the experimental temperatures indicating that nucleophilic solvation is entropy controlled.

The good Hammett correlation of log k_{solv} for equilibrium formation of the *a*-azido benzyl carbocations from neutral azide ion adducts with s^+ substituent constants[22] ($r_{solv}^+ = -3·91$) which is consistent with large development of positive charge at the benzylic carbon in the rate-determining transition state for solvolysis, shows that the thermodynamic stability of cations is sensitive to the polar effects of the substituents to a large extent. A similar good Hammett correlation is also observed for log k_s of addition of water to *a*-azido benzyl carbocations ($r_s^+ = 2·02$). But the large reduction (@ 50%) in the magnitude of r_s^+ (irrespective of the sign) is again due to large reduction in the effective positive charge at the benzylic portion of the cation, by effective delocalization of charge onto the electron-donating *a*-azido group.

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