Substituent effects on the spontaneous cleavage of benzyl-gem-dibromides in aqueous solution

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The α-bromobenzyl cations have been produced in aqueous solution by chemical initiation (solvolysis) of benzylα-gem-dibromides. The solvolysis reactions of benzylα-gem-dibromides in water proceed by a stepwise mechanism through α-bromobenzyl carbocation intermediates, which are captured by water to give the corresponding benzaldehydes as the sole detectable products. Rate constant ratios between reaction with bromide ion and reaction with water have been determined by analysis of bromide common ion inhibition of the solvolysis reaction. The rate constants, k, of the α-bromobenzyl cations, activation parameters for solvolysis step and for addition of water to the cation are some of the salient features not reported earlier. Effect of substituents is also discussed in terms of limited reaction of bromide ion with benzyl carbocations.

Experimental

Inorganic salts and organic chemicals used for chemical syntheses were reagent grade and used as such. The water used for kinetic studies was distilled over acid dichromate and permanganate. The gem-dibromides were synthesized as per a reported procedure. Solvolysis rate constants for the reaction of the benzyl-gem-dibromides were determined in water containing 1% acetonitrile at 25°C and at a constant ionic strength of 1.0 M, maintained with NaClO₄. The stock solution of the substrate was prepared in acetonitrile. The solvolysis reactions of benzyl-gem-dibromides were initiated by making a 100-fold dilution of the stock solution of substrate in acetonitrile to the reaction mixture to give a final concentration of 1.0 × 10⁻⁴ M by injecting 30 µL to 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 λ_max of the reactant and that of the product as well. Such absorption spectra were first recorded for all the benzyl-gem-dibromides. Thus by knowing λ_max of all the ring substituted benzaldehydes from the time dependent UV-visible absorption spectrum, the kinetics were followed spectrophotometrically by monitoring the appearance of corresponding benzaldehydes at their λ_max. All spectrophotometric experiments were performed on UVIKON 923 UV-vis spectrophotometer, which was supplied with necessary software for performing the experiments, storing and analyzing the experimental data. KaleidaGraph supplied by Synergy Software, USA, was used to carry out the analysis of the experimental data. Running the UV-vis spectrum of the authentic benzaldehydes identified the products as corresponding benzaldehydes.

Results and discussion

The solvolysis reactions of benzyl-gem-dibromides in water at 25°C and I = 1.0 M (NaClO₄) gave the corresponding benzaldehydes as the sole detectable product (99%). First order solvolysis rate constants for these reactions in the absence of bromide ion, k_solv, (s⁻¹) were determined by monitoring the appearance of corresponding benzaldehydes by UV spectroscopy.
The dependence of the normalized rate constant ratios, \( k_{\text{obsd}}/k_{\text{act}} \), for benzyl-gem-dibromide on the concentration of added bromide ion (where \( k_{\text{obsd}} \) was the observed rate constant at a given concentration of bromide ion and \( k_{\text{act}} \) was the rate constant in the absence of added bromide ion) was determined. The bromide ion inhibition showed that the reactions of benzyl-gem-dibromide proceeded by a stepwise mechanism, through the diffusionally equilibrated \( \alpha \)-bromobenzyl carboxylation that could be trapped competitively by added bromide ion and solvent water (Scheme 1).

This kind of common ion inhibition on the solvolysis rates was observed for all the starting compounds studied and followed Eq. (1) derived for the mechanism shown in Scheme 1.

\[
\frac{k_{\text{solv}}}{k_{\text{act}}} = 1 + \left( \frac{k_{br}}{k_{s}} \right) [\text{Br}^-]
\]  

(1)

There was no detectable lag in the formation of corresponding benzaldehyde, which showed that there was no accumulation of the intermediate bromohydrins (Br-1-OH, Scheme 1), whose reactivities of which were therefore much greater than those of the parent benzyl-gem-dibromide (Br-1-Br). In no case was there any detectable formation of the ring substituted N-(\( \alpha \)-bromobenzyl)acetamide 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 \( \mu \)L of this solution was used for initiating the reaction; this gave approximately 0.19 \( M \) of acetonitrile in solution). This showed that the pseudo-first order rate constants for the reaction of the bromobenzyl carboxylations with solvent water, \( k_{br} \), were much higher than those for the Ritter type reaction. The common ion inhibition of the solvolysis of the benzyl-gem-dibromide by added bromide ion provided classic evidence for a stepwise 16,17 mechanism, with a rate determining cleavage of benzyl-gem-dibromides to form diffusionally-equilibrated carboxylation reaction intermediates (which could be trapped by bromide ion and by solvent). The capture of \( \alpha \)-bromobenzyl carboxylations by added bromide ion resulted in a reduction in their steady state concentration, and hence in \( k_{\text{obsd}} \) for solvolysis of the starting benzyl-gem-dibromides. The good fit to Eq. 1 of the kinetic data for solvolysis of benzyl-gem-dibromides, in the presence of increasing concentration of bromide ion, showed that the reactions proceeded through liberated carboxylation intermediates. For example, from the plot of \( k_{\text{act}}/k_{\text{obsd}} \) versus [\( \text{Br}^- \)] the value of \( k_{br}/k_{s} \) was obtained for benzyl-gem-dibromide. Therefore, absolute rate constants \( k_{br}/k_{s} \) (s\(^{-1}\)) for capture of \( \alpha \)-bromobenzyl carboxylations by water were obtained from the rate constant ratios \( k_{br}/k_{s} (M^{-1}) \) for partitioning of the cations and using a value for \( k_{br} (5 \times 10^8 M^{-1}s^{-1}) \) for the reaction of cation with \( \text{Br}^- \).

Activation parameters for the solvolysis step \( (k_{\text{obsd}}) \) were determined by measuring the rate constants at four different temperatures and plotting log \( k_{\text{obsd}}/T \) against 1/T using Eyring equation\(^{18}\). For the step of addition of water to the cation \( (k_{br}) \), first the common bromide ion inhibition was studied on \( k_{\text{obsd}} \) with increase in concentration of bromide ion at constant ionic strength of 1.0 \( M \) (NaClO\(_4\)). Similarly \( k_{br} \) values were determined at four different temperatures. Again the activation parameters were determined for \( k_{br} \) as above. All the activation parameters along with \( k_{\text{obsd}}, \) selectivity \( (k_{br}/k_{s}) \) and \( k_{s} \) have been given in Table 1.

There was a 2,500-fold increase in \( k_{\text{obsd}} \) for benzyl-gem-dibromides as the ring substituent \( Y \) was changed from 3-F to 4-MeO (Table 1), which was consistent with a large development of positive charge at the benzylic carbon in the rate-determining transition state for solvolysis. Therefore, it was evident that electron-donating groups like MeO present in benzylic cations would stabilize the cations, and electron-withdrawing groups like F would destabilize the cations.

Hammett correlation of log \( k_{\text{obsd}} \) for equilibrium formation of the \( \alpha \)-bromobenzyl carboxylations from the neutral bromide ion adducts with \( \sigma \) substituent constants\(^{19}\) (\( \rho_{\text{obsd}} = -5.49 \)) was consistent with a large development of positive charge at the benzylic carbon in the rate-determining transition state for solvolysis. This showed that the thermodynamic stability of cations was sensitive to the polar effects of the substituents to a larger extent. Similarly, a Hammett correlation was also observed for log \( k_{br} \) for addition of water.
Table 1 — Solvolysis of benzyl-gem-dibromides in aqueous solution at 25°C and I = 1.00 M (NaClO₄)

<table>
<thead>
<tr>
<th>Y</th>
<th>k_{sol}/s⁻¹</th>
<th>k_{b}/k_{s} (M⁻¹)</th>
<th>k_{b}/s⁻¹</th>
<th>σ</th>
<th>ΔH_{sol}⁻¹ (kJ/mol)</th>
<th>ΔS_{sol}⁻¹ (J/K/mol)</th>
<th>ΔH_{sol}为一体</th>
<th>ΔS_{sol}为一体</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-CH₃</td>
<td>0.186</td>
<td>10</td>
<td>5.00 × 10⁴</td>
<td>-0.28</td>
<td>56.6</td>
<td>-9.80</td>
<td>7.03</td>
<td>-109</td>
</tr>
<tr>
<td>4-H</td>
<td>5.17 × 10⁻⁴</td>
<td>0.9</td>
<td>5.60 × 10⁴</td>
<td>0.00</td>
<td>74.2</td>
<td>-6.70</td>
<td>8.25</td>
<td>-22.8</td>
</tr>
<tr>
<td>3-F</td>
<td>7.32 × 10⁻⁵</td>
<td>The cation is too short-lived to determine common ion effect</td>
<td>0.34</td>
<td>95.1</td>
<td>-4.80</td>
<td>Could not be determined due to high reactivity of the cation with water</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Comparison of ρ in the solvolysis and addition of water in benzyl-gem-dichlorides and dibromides: The ρ values for solvolyses of benzyl-gem-dichlorides⁴¹ and dibromides were −2.05 and 1.17 while for the addition of water to the corresponding cations, the ρ values were −5.49 and 3.74 respectively.

These Hammett substituent constants depend largely on the stabilities of the intermediate α-chloro and α-bromo substituted benzyl carboxations that is their formation from the neutral halide ion adducts and their reaction with nucleophile (water). The intrinsic barrier for capture of resonance-stabilized carboxations by nucleophiles results largely from loss of resonance interactions in the transition state by bond formation to the nucleophile. The lower intrinsic barrier for formation and larger intrinsic barrier for capture of α-bromo benzyl carboxations by solvent water (than of the α-chloro stabilized benzyl carboxations) was consistent with the fact that the α-bromo substituted benzyl carboxations were more stable than those of their chloro analogs. This was due to more polarizability and the larger size of bromo substituent, as compared to the chloro substituent. Hence, the Hammett ρ values for both the processes were higher for bromobenzyl carboxations.

Acknowledgement

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References