Studies in Nucleophilic Substitutions: Part I—Reactions between Phenylmethylcarbinols & Hydrobromic Acid & Structure-Reactivity Analysis

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The kinetics of the reactions of phenylmethylcarbinol (PMC) and substituted PMCs with hydrobromic acid have been studied in 100% acetic acid. The reaction rate follows total second order, first order each in [PMC] and [HBr]. The effect of substituents in the phenyl ring on the rate of substitution has been studied. The analysis of the rate data in terms of the Hammett equation gives a concave-down type of curve, though the Exner plot is linear. A stepwise mechanism involving the equilibrium formation of the conjugate acid of the alcohol followed by an attack by Br\(^{-}\) accounts for the observed structure-reactivity pattern.

Hydrogen halides have been used since long for the preparation of halo compounds from alcohols (see Eq. 1).

\[
\text{ROH} + \text{H}^+ + \text{Br}^- \rightarrow \text{R} \cdot \text{Br} + \text{H}_2\text{O}
\]  

(1)

The displacement reaction (Eq. 1) in the second stage can proceed either by an \(S_{N1}\) or an \(S_{N2}\) process, depending on the nature of the alcohol. However, it is suggested that all substitution reactions at a saturated carbon proceed by a single mechanism accommodating these extremes. We present in this note some interesting results of the effect of structural variations in phenylmethylcarbinol (PMC) on its reactivity towards HBr.

Hydrobromic acid (AR, 48%, v/v) was redistilled and the fraction distilling at 125-26°C was used for the kinetic experiments. The commercially available, pure phenylmethylcarbinols were distilled before use. Acetic acid, purified by the usual procedure, was used as the reaction medium. As the reaction between HBr and PMC was extremely sluggish at lower temperatures, the reactions were conducted between 70° and 90°. Sufficient care was taken to minimise evaporational losses and appropriate corrections were made for any solvent loss by running concurrent blank experiments. All reactions were carried out under bimolecular conditions with equimolar concentrations of reactants and the specific rate constants were calculated from the integrated second order expression. The reaction products were identified as the corresponding alkyl bromides by preparative TLC. There was virtually no conversion of the alcohols to acetates under the conditions of the experiments. It has also been shown that the rate of reaction of methanol with HBr is faster by a factor of 100 than the rate of esterification by acetic acid.

The reactions between HBr and PMC and substituted PMCs follow excellent second order kinetics, showing that despite the secondary alcohol being used, the reaction is essentially an \(S_{N2}\) type. Further, initially added bromide ions do not have any significant retarding effect on the rate of reaction. Also, addition of water to the solvent acetic acid produces a perceptible decrease in rate. The second order rate constants for the displacement reactions of PMC and the substituted PMCs and the activation parameters are given in Table 1.

It is interesting to note that, irrespective of the nature of the substituent in the phenyl ring, the substituted PMCs react at a slower rate, as compared to the parent compound. These data when cast in the form of a Hammett plot, show a concave-down type of curve. While such deviations from the Hammett plot are not unusual, the present results are the first of its kind in an alcohol-HBr reaction.

The observed shape of the Hammett plot (Fig. 1) may arise for a reaction, the mechanism of which involves a reversible step followed by an irreversible

<table>
<thead>
<tr>
<th>R - C₆H₄</th>
<th>(10^2 \frac{k}{T}) (dm³mol⁻¹ min⁻¹)</th>
<th>(E_a) (kJmol⁻¹)</th>
<th>(\Delta H^\ddagger) (kJmol⁻¹)</th>
<th>(\Delta S^\ddagger) (JK⁻¹ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>14.4</td>
<td>82.0</td>
<td>79.1</td>
<td>39</td>
</tr>
<tr>
<td>p-Cl</td>
<td>6.47</td>
<td>74.1</td>
<td>71.1</td>
<td>67</td>
</tr>
<tr>
<td>m-Cl</td>
<td>1.33</td>
<td>78.7</td>
<td>75.8</td>
<td>67</td>
</tr>
<tr>
<td>p-Br</td>
<td>4.36</td>
<td>84.1</td>
<td>81.6</td>
<td>42</td>
</tr>
<tr>
<td>m-Br</td>
<td>1.59</td>
<td>75.7</td>
<td>74.5</td>
<td>71</td>
</tr>
<tr>
<td>p-F</td>
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<td>63.1</td>
<td>60.7</td>
<td>105</td>
</tr>
<tr>
<td>m-F</td>
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<td>63.2</td>
<td>60.7</td>
<td>100</td>
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<tr>
<td>p-Me</td>
<td>5.67</td>
<td>77.0</td>
<td>74.1</td>
<td>54</td>
</tr>
<tr>
<td>m-Me</td>
<td>10.1</td>
<td>77.0</td>
<td>74.1</td>
<td>54</td>
</tr>
</tbody>
</table>

*Values at 80°
one leading to the products. If the observed rate constant is effectively the product of the equilibrium constant for the first step (Eq. 2) and the rate constant for the second step (Eq. 3), two consequences may arise. One is the mutual cancellation of polar effects (as in the acid-catalysed esterification of benzoic acids in methanol or a concave-down type of curve as in the present case). For

\[
R - C_6H_4 - \text{CHOH} - CH_3 + H^+ \xrightleftharpoons{k_1}{k_1^{-1}} R - C_6H_4 - \text{CHOH}_2 - CH_3
\]  
\[
R - C_6H_4 - \text{CHOH}_2 - CH_3 + \text{Br} \xrightarrow{k_2} H_2O + R - C_6H_4 - CHBr - CH_3 \quad (3)
\]

such a situation, an electron-releasing substituent (such as p-CH_3) might facilitate the formation of the oxonium ion but would slow down the subsequent decomposition \((k_2 \leq k_1^{-1})\), resulting in a rate lower than that of PMC itself. Similarly an electron-withdrawing substituent might make even the equilibrium formation of the conjugate acid the slow one \((k_1 \geq k_2)\). The interplay of such effects might lead to the apparent breakdown of the Hammett relationship. Although the above formulation envisages discrete formation of an oxonium ion the more attractive alternative, consistent with the low polarity of the solvent system, is the formation of a hydrogen-bonded complex between PMC and HBr in the first step (Eq. 4).

The activation parameters \(E_a\) and \(\Delta S^\ddagger\) obtained for these reactions are of the right order of magnitude for bimolecular nucleophilic substitution reactions. It is also observed that these reactions are neither isoentropic nor isoenthalpic in nature. It is therefore of interest to subject these data to an Exner analysis\(^4\) by plotting \(\log k_{T_2}\) against \(\log k_{T_1}\) \((T_2 > T_1)\). A fair correlation is obtained and the resulting linear plot has a slope \(b > 1\), indicating that the reaction under study belongs to the class of 'compensated' reactions. This appears to be the first instance where a reaction series fails to obey Hammett relationship but the Exner plot is found linear. In the formation of semicarbazones of carbonyl compounds of related structure (where the reaction goes in at least two steps), Hammett and Price\(^4\) were unable to establish any isokinetic relationship (between \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\)). Leffler and Grunwald\(^5\) considered that the failure of the isokinetic relationship provided evidence for the involvement of more than one mechanism by which a substituent
interacted with the reaction site. However, in the present investigation, the reaction that proceeds by a multistep pathway with different rate-determining steps, seems to obey the isokinetic relationship.

References
4 Price F P (Jr), Hammett L P. J Am chem Soc. 63 (1941) 2387.