The Rate Constants for the Reactions of 4-Nitrophenyl Radical with Halide Ions. A Reversal in Nucleophilic Reactivity

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It is a generally accepted conclusion that the order of nucleophilicity of halide ions in dipolar aprotic solvents is \( \text{Cl}^- > \text{Br}^- > \text{I}^- \).\(^1\) This reactivity order has been observed in \( S_n2 \) displacement reactions in \( N,N\)-dimethylformamide (DMF),\(^2\) acetone,\(^3\) dimethylsulfoxide,\(^4\) acetonitrile,\(^5\) molten salts\(^6,^7\) and in the gas phase (for \( \text{Cl}^- \) and \( \text{Br}^- \)).\(^8,^9\) The reversal in reactivity as compared to that in polar protic solvents is attributed to differences in solvation energies.\(^1\)

\[
\text{Ar}^+ \text{X}^- \rightarrow \text{Ar}^- \text{X}^- \quad (1)
\]

The reactions between aryl radicals and nucleophiles, a key step in the \( S_n2 \) mechanism,\(^10\) should represent an ideal case for reactivity studies. The reactions (eqn. (1)) involve the formation of a single bond without any accompanying bond breaking. The factors expected to play deciding roles in determining the rates of reactions (1) are the changes in solvation between the nucleophile and the activated complex and the strength of the bond being formed in the transition state. If \( \text{X}^- \) is halide and the solvent DMF, both of the factors would appear to suggest that the reactivity order is expected to be \( \text{Cl}^- > \text{Br}^- > \text{I}^- \).

Aryl radicals can be conveniently generated by the reduction of the corresponding diazoniun ion with iodide in aprotic solvents.\(^11\) In DMF in the presence of nucleophiles the aryl radical formed in (2) partitions between reactions (3) to (6). The absolute rate constant for reaction (6), which is diffusion controlled,\(^12\) can be calculated and all other rate constants can then be determined from product distributions when the reactions are conducted in the presence of excess \( \text{X}^- \). Since there is some uncertainty in the estimation of \( k_6 \), we can use an approximate value of \( 10^{10} \text{ M}^{-1} \text{s}^{-1} \) as a reasonable estimate.

\[
\begin{align*}
\text{Ar}^- \text{N}_2^+ + \text{I}^- & \rightarrow \text{Ar}^+ \text{N}_2 + \frac{1}{2} \text{I}_2 \\
\text{Ar}^+ + \text{SH (DMF)} & \rightarrow \text{Ar}^- + \text{H} + \text{S} \\
\end{align*}
\]

Experiments were carried out in which equimolar amounts of \( \text{Ar}^- \text{N}_2^+ \) (\( \text{Ar} = p\text{-nitrophenyl} \)) and \( \text{I}^- \) were allowed to react in the presence of an excess of \( \text{I}_2 \) in DMF. The relative rates of reactions (3) and (6) could then be determined from the mol ratios, \( n(\text{Ar}^- \text{H})/n(\text{Ar}^- \text{I}) \) of the products and \( n(\text{DMF})/n(\text{I}_2) \) of the reactants, assuming that reaction (5) contributed negligibly to the formation of \( \text{Ar}^- \text{I} \) under the reaction conditions. Using a value of \( 10^{10} \text{ M}^{-1} \text{s}^{-1} \) for \( k_6 \), a value of \( 6 \times 10^6 \text{ M}^{-1} \text{s}^{-1} \) was estimated for \( k_3 \). Other rate constants could then be estimated using eqn. (8) where \( \text{X}^- \) is halide reacting in reactions (4) or (5), when \( \text{X}^- = \text{I}^- \), the conditions were such that reaction (6) did not contribute significantly to the formation of \( \text{Ar}^- \text{I} \).

\[
k_{x^-} = n(\text{Ar}^- \text{X})/n(\text{Ar}^- \text{H})[n(\text{DMF})/n(\text{X}^-)]k_3 \quad (8)
\]

For reactions carried out in DMF at 22°C are summarized in Table I. In the absence of tetraalkylammonium ions the rate constants for the reactions of \( \text{I}^- \), \( \text{Br}^- \) and \( \text{Cl}^- \) with 4-nitrophenyl radical were estimated to be equal to \( 5.0 \times 10^8 \), \( 5.5 \times 10^8 \) and \( 2.8 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \), respectively. Of the alkali metal salts used, both \( \text{K} \) and \( \text{KBr} \) are expected to be completely dissociated in DMF while some association of \( \text{LiCl} \) is to be expected. \( \text{LiNO}_3 \) is more highly associated in DMF than \( \text{LiCl} \).\(^4\) In the presence of excess \( \text{Bu}_4\text{NNO}_3 \), which would be expected to free any \( \text{Cl}^- \) associated with \( \text{Li}^+ \), the observed rate constant was slightly lower which indicates that ion association is not a complicating factor in any of the reactions. In general, the calculated rate constants are somewhat lower in the presence of tetraalkylammonium ions. The reason for this is not clear. A possible reason, that the tetraalkylammonium ions serve as hydrogen atom donors in reaction (3), can be ruled
Table 1. Relative rate constants for the reactions of 4-nitrophenyl radical with halide ions in N,N-dimethylformamide.

<table>
<thead>
<tr>
<th>MX(mmol) b</th>
<th>R₄NX(mmol) b</th>
<th>ArH/ArX c</th>
<th>kₖₑₐ₁ d</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI (0.50)</td>
<td></td>
<td>0.336</td>
<td>1.000</td>
</tr>
<tr>
<td>KI (0.50)</td>
<td>Et₄NBF₄ (0.50)</td>
<td>0.366</td>
<td>0.918</td>
</tr>
<tr>
<td>KI (0.50)</td>
<td>Et₄NBF₄ (1.00)</td>
<td>0.418</td>
<td>0.804</td>
</tr>
<tr>
<td>KBr (0.50)</td>
<td></td>
<td>3.19</td>
<td>0.105</td>
</tr>
<tr>
<td>KBr (0.50)</td>
<td>Et₄NBF₄ (0.25)</td>
<td>3.12</td>
<td>0.108</td>
</tr>
<tr>
<td>KBr (0.50)</td>
<td>Et₄NBF₄ (0.50)</td>
<td>3.35</td>
<td>0.100</td>
</tr>
<tr>
<td>KBr (0.50)</td>
<td>Et₄NBF₄ (1.00)</td>
<td>347.0</td>
<td>0.0968</td>
</tr>
<tr>
<td>—</td>
<td>Et₄NBr (0.50)</td>
<td>3.63</td>
<td>0.0926</td>
</tr>
<tr>
<td>LiCl (2.50)</td>
<td></td>
<td>12.1</td>
<td>0.0055</td>
</tr>
<tr>
<td>LiCl (2.50)</td>
<td>Bu₄NNO₃ (1.00)</td>
<td>15.9</td>
<td>0.00423</td>
</tr>
<tr>
<td>—</td>
<td>Bu₄NI (1.00)</td>
<td>0.431</td>
<td>0.390</td>
</tr>
</tbody>
</table>

*The radical was generated by the reduction of 4-nitrophenylidiazonium ion by iodide ion according to Ref. 11. bThe salts were dissolved in DMF (10.0 ml) under N₂ before adding the diazonium salt (0.05 mmol) in DMF (1.0 ml). cThe ratio of products was determined by GLC. dThe relative rate constants for the reaction between the radical and the halide ions were calculated from the product distribution.

out on the basis that the effect of a given concentration of Et₄N⁺ on the rate of reaction (6) is the same for I⁻ as Br⁻. According to the relative rates the effect would be expected to be an order of magnitude greater with Br⁻ as the nucleophile.

The relative rate constants for the reactions of the halide ions with 4-nitrophenyl radical are compared with Swain-Scott nucleophilicity constants in Table 2. The values of rate constants obtained with alkali metal counter ions compare very closely with the nucleophilicity constants. A nearly exact comparison is found for chloride with iodide when Bu₄N⁺ was the counter ion.

The relative rates of reactions of the halide ions can be rationalized in terms of orbital interactions if the initial interaction between the radical and the halide ion involves the lowest energy unoccupied π molecular orbital of the radical and the highest energy occupied orbital of the halide ions. The most favorable interaction is that between iodide and the radical. This suggests 1 for the structure of the transition state for these reactions. Structure 1 implies that in the transition state the p orbital on the carbon in the 4-position is not overlapping effectively with the rest of the π system as rehybridization begins to take place. Transition state 1 also provides an explanation of the higher reaction rates in the presence of alkali metal cations. Ion association at the oxygens of the nitro group would favor the dipolar structure.

The possibility that nucleophilic reactions of halide ions with Ar−N₃⁺ contribute to the formation of Ar−X can be ruled out from the fact that no reaction is observed, during the time scale of the measurements, between Cl− and Br− and Ar−N₃⁺ when I− is excluded from the reaction mixture. Neither Cl− nor Br− are capable of reducing Ar−N₃⁺ at a significant rate.

It is well known that nucleophilicity depends upon the type of reaction under consideration. Differences in nucleophilicity can often be explained using frontier orbital theory. The results reported here indicate that the aryl radicals are soft electrophiles reacting most rapidly with polarizable soft nucleophiles.

Table 2. Comparison of the relative rate constants with nucleophilicity constants of the halide ions.

<table>
<thead>
<tr>
<th>Halide a</th>
<th>(10⁶) b</th>
<th>kₖₑ₁ c</th>
<th>kₖₑ₁ d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>0.01</td>
<td>0.005</td>
<td>0.011</td>
</tr>
<tr>
<td>Bromide</td>
<td>0.063</td>
<td>0.105</td>
<td></td>
</tr>
<tr>
<td>Iodide</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*Data taken from Table 1. aThe nucleophilicity constants are from Ref. 15. cValue refers to experiments with only alkali metal halides. dFrom experiments on solutions containing Bu₄N⁺ (0.1 M).

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