AROMATIC NUCLEOPHILIC SUBSTITUTIONS.
REACTIONS OF HALOGENO AND NITRO-
SUBSTITUTED BENZENES—PART II*

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ABSTRACT

The kinetics of the reaction of 2, 4-dinitro-1-bromo benzene and
2, 4-dinitro-1-iodo benzene with various aromatic bases has been studied in
alcohol, alcohol-acetonitrile, alcohol-dimethylformamide and alcohol-
dimethyl sulfoxide mixtures. The halogen order observed is Br > Cl > I.
No base catalysis has been observed under these conditions. ρ values
have been computed. Mechanism of the aromatic nucleophilic substi-
tution is discussed.

INTRODUCTION

In a previous communication¹ we reported the reactions of 2, 4-dinitro-1-
chloro benzene with various aromatic bases in alcohol, alcohol-dimethyl sulf-
oxide, alcohol-dimethylformamide and alcohol-acetonitrile mixtures. This
communication deals with reactions of 2, 4-dinitro-1-bromo benzene and
2, 4-dinitro-1-iodo benzene.

EXPERIMENTAL

Materials.—All
the
bases
used
were
obtained
from
British
Drug
House
(BDH)
and
were
purified
and
distilled
before
use
as
reported
earlier (loc. cit.). The substrates were prepared.² The physical constants of
the compounds
are
as
follows.

2, 4-dinitro-1-bromo benzene, m.p. 73°C, 2, 4-dinitro-1-iodo benzene,
m.p. 89°C, m-nitroaniline, m.p. 114°C, p-nitroaniline, m.p. 147°C, o-nitro
aniline, m.p. 71°C, aniline, b.p. 183°C, p-toluidine, m.p. 45°C, m-toluidine,
b.p. 199°C, p-chloroaniline, m.p. 70°C.

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Kharagpur during 27th to 31st December, 1969.

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Acetonitrile, dimethylformamide and dimethyl sulfoxide were of BDH AR/grade and were used without further purification. Alcohol was of absolute grade. Second order rate constants were calculated by using least square method.

**Preparation of materials and rate measurements.**—Preparation of indicator, solutions and rate measurements were as described earlier (*loc. cit.*).

1. The products of the reaction are 2, 4-dinitro-diphenylamines. In the alcohol medium alone, there is precipitation of the product towards the end of the reaction. Reactions can be followed in most of the cases till 70% of the reaction. The \( p \)- and \( o \)-nitroanilines do not react, only \( m \)-nitroaniline reacts, that too very sluggishly.

2. There is no drift in the rate constants as the reaction proceeds especially in the mixtures where homogeneity is perfectly maintained. Even

**Table I**

*Second order rate constants \( k \ (l. \text{ mole}^{-1} \text{ min}^{-1}) \times 10^3 \)*

<table>
<thead>
<tr>
<th>Solvent mixtures (80 : 20% v/v)</th>
<th>Substrate : 2, 4-dinitro-1-bromo benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base</strong></td>
<td><strong>Ratio Substrate : Base</strong></td>
</tr>
<tr>
<td>Aniline</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Aniline</td>
<td>1 : 2</td>
</tr>
<tr>
<td>Aniline</td>
<td>1 : 3</td>
</tr>
<tr>
<td>( p )-Toluidine</td>
<td>1 : 3</td>
</tr>
<tr>
<td>( m )-Toluidine</td>
<td>1 : 3</td>
</tr>
<tr>
<td>( p )-Chloroaniline</td>
<td>1 : 3</td>
</tr>
<tr>
<td>( m )-Nitroaniline</td>
<td>1 : 3</td>
</tr>
<tr>
<td>( p )-Nitroaniline</td>
<td>1 : 3</td>
</tr>
<tr>
<td>( o )-Nitroaniline</td>
<td>1 : 3</td>
</tr>
</tbody>
</table>
in alcohol there is no drift till 60% of the reaction and only in this medium there is precipitation of the product towards the end.

The concentration ranges are \(0.025\, \text{M}\) and \(0.025\, \text{M}-0.075\, \text{M}\) for the substrate and amines respectively. There is no solvolysis because we have kept blanks always which have been checked in alcohol, alcohol-DMF, alcohol-DMSO and alcohol-\(\text{CH}_3\text{CN}\) mixtures and also in DMF, DMSO and \(\text{CH}_3\text{CN}\). Hence there is no solvolysis under these conditions.

Irrespective of concentration the rate constants are almost similar within experimental error.

RESULTS AND DISCUSSION

The second order rate constants of the bromo and iodo derivatives in various solvent mixtures are given in Tables I–III.

**Table II**

*Second order rate constants* \(k \left( l.\, \text{mole}^{-1}\, \text{min.}^{-1} \right) \times 10^3\)

<table>
<thead>
<tr>
<th>Solvent mixtures (80 : 20% v/v)</th>
<th>Temp. 50° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate : 2, 4-dinitro-1-iodo benzene</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Base</th>
<th>Ratio Substrate : Base</th>
<th>Alcohol-DMSO</th>
<th>Alcohol-DMF</th>
<th>Alcohol</th>
<th>Alcohol-Aceto-nitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>1 : 1</td>
<td>8.247</td>
<td>7.005</td>
<td>6.779</td>
<td>4.30</td>
</tr>
<tr>
<td>Aniline</td>
<td>1 : 2</td>
<td>8.316</td>
<td>7.28</td>
<td>6.353</td>
<td>4.12</td>
</tr>
<tr>
<td>Aniline</td>
<td>1 : 3</td>
<td>8.886</td>
<td>7.98</td>
<td>6.826</td>
<td>4.548</td>
</tr>
<tr>
<td>p-Toluidine</td>
<td>1 : 3</td>
<td>34.42</td>
<td>27.53</td>
<td>23.83</td>
<td>13.81</td>
</tr>
<tr>
<td>m-Toluidine</td>
<td>1 : 3</td>
<td>13.14</td>
<td>11.48</td>
<td>9.71</td>
<td>6.65</td>
</tr>
<tr>
<td>p-Chloroaniline</td>
<td>1 : 3</td>
<td>2.58</td>
<td>1.667</td>
<td>1.628</td>
<td>1.38</td>
</tr>
</tbody>
</table>

As found with chloro derivative, the reactions are second order without any amine catalysis under the conditions studied. The following facts emerge from the experimental results:

1. The halogen order found is \(\text{Br} > \text{Cl} > \text{I}\) in all the solvent mixtures studied.
2. The solvent effect is Alcohol-DMSO > Alcohol-DMF > Alcohol > Alcohol-Acetonitrile.

3. The \( \rho \) values for the substrate 2, 4-dinitro-1-bromo benzene in solvent mixtures alcohol-DMSO, alcohol-DMF, alcohol and alcohol-acetonitrile are \(-2.95\), \(-3.07\), \(-2.6\) and \(-2.75\) and for 2, 4-dinitro-1-iodo benzene \(-2.8\), \(-3.0\), \(-2.8\) and \(-2.6\) respectively.

4. There has been found precipitation of the product in pure alcohol whereas in mixtures of DMF, DMSO and acetonitrile the reactions are homogeneous.

5. A glance at the tables makes it clear about the absence of amine catalysis.

**TABLE III**

*Second order rate constants \( k \left( l. \text{ mole}^{-1} \text{ min}^{-1} \right) \times 10^8 \)*

<table>
<thead>
<tr>
<th>Solvent mixtures: (80 : 20% v/v)</th>
<th>Temp. 50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base : Aniline</td>
<td></td>
</tr>
<tr>
<td>Substrate</td>
<td>Ratio Substrate: Base</td>
</tr>
<tr>
<td>2, 4-Dinitro-1-chloro benzene 1 : 3</td>
<td>23.86</td>
</tr>
<tr>
<td>2, 4-Dinitro-1-bromo benzene 1 : 3</td>
<td>32.13</td>
</tr>
<tr>
<td>2, 4-Dinitro-1-iodo benzene 1 : 3</td>
<td>8.886</td>
</tr>
</tbody>
</table>

It is immediately obvious from the tables that the order found Br > Cl > I is the same as that for reactions of \( o \)- and \( p \)-nitro phenyl halides with piperidine in ethanol and of 2, 4-dinitro phenyl halides with piperidine in methanol and with aniline in ethanol and it is clearly determined largely by the polarisation of C–X bonds.\(^3\) The dependence on the polarisation of bond between carbon and the displaceable group is borne out by the work of Parker and Read\(^4\) with picryl halides, 1, 2, 3, 5-tetranitro benzene and 1, 2, 4-trinitro benzene with aniline in ethanol. It appears that a two-stage mechanism in which the decomposition of the intermediate has become rate-determining is unlikely. The possibilities are a two-stage mechanism in which the formation of the intermediate is still largely rate determining or
a one-stage mechanism. The structural effects point to a rate-determining bond formation. \( p \)-Nitro aniline did not react indicating that bond formation is rather important. It is necessary to explain why the order of displacement is \( \text{Br} > \text{Cl} > \text{I} \) and not \( \text{Cl} < \text{Br} < \text{I} \) as found in aliphatic nucleophilic substitution reactions which go by a concerted process. The greater reactivity of the bromide over chloride cannot be due to bond strength effects. The only reasonable explanation is that of Bunnett who has postulated an accelerative London force interaction between the reagent and the displaced group. This will be greater for bromine than for less polarisable chlorine. The evidences that are usually advanced for an intermediate complex mechanism are\(^6\), (1) Synthetic evidences, (2) Evidence from electrochemistry, (3) Cryoscopic measurements in ethanolamine, (4) Evidence from deuterium exchange experiments, and (5) Evidence from spectroscopy.

There is enough proof against a rate-determining decomposition of the intermediate especially the absence of deuterium effect as proved with reactions of 2,4-dinitro-1-chloro benzene with \( n \)-butyl amine and \( N \), \( N \)-di-deuterio-\( n \)-butyl amine containing 0·75\% ethanol (\textit{loc. cit.}). Many explanations have been advanced to rationalise the absence of deuterium effect with rate-determining decomposition of the intermediate. One such has been the postulate that the rate-determining step is a concerted process including breaking or partial breaking of the \( N - H \) bond together with breaking of the \( C - Cl \) bond. Though it is a possibility, it is unlikely. It is more realistic to think of an intermediate complex mechanism with a rate-determining bond formation, or a simple one-stage mechanism in which small amount of bond stretching has taken place in the formation of the transition state. A reference to the energy profile diagrams described by Parker and Read (\textit{loc. cit.}) makes this clear.

On the basis of leaving group tendencies and on the basis of solvent effect with dipolar aprotic solvents Parker\(^6\) has established that there is virtually no —ve charge on the leaving halogen in the aromatic nucleophilic substitution reactions. Hence a two-stage mechanism with a rate-determining bond formation is more likely. The difference in the halogen order is due to the superimposition of polarizability effects and this also supports the two-step mechanism with a rate-determining bond formation to which must be added the polarizability effect of Bunnett.\(^7\)

\textit{Effect of solvent.}—As reported earlier for the chloro-derivative, the order of solvent influences is alcohol-DMSO \( > \) Alcohol -DMF \( > \) Alcohol \( > \) Alcohol-Acetonitrile. The fastness in DMSO mixtures might be that DMSO
molecules in or arranged about the transition state for a reaction in DMSO-alcohol mixtures, lower the free energy of the transition state, relative to that for reaction in pure alcohol. In the two-step mechanism of aromatic nucleophilic substitution reaction, with primary and secondary aromatic amines, the transition state is a much stronger H-bond donor than the reactant amine.

It is notable that DMSO is a stronger base and probably a stronger H-bond acceptor than alcohol. These cumulatively are responsible for the high rate observed in DMSO-alcohol mixtures.

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3a. Chapman, N. B., Parker, R. E. and Soanes, P. W.

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4. Parker, R. E. and Read, T. O.
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7. Bunnett, J. F.

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