The Rate Constants for the Reactions of 4-Nitrophenyl Radical with Halide Ions. A Reversal in Nucleophilic Reactivity
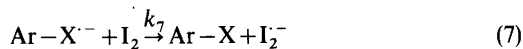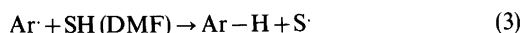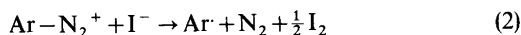
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It is a generally accepted conclusion that the order of nucleophilicity of halide ions in dipolar aprotic solvents is $Cl^- > Br^- > I^-$.[1] This reactivity order has been observed in S_N2 displacement reactions in N,N-dimethylformamide (DMF),[2] acetone,[3] dimethylsulfoxide,[4] acetonitrile,[5] molten salts[6,7] and in the gas phase (for Cl^- and Br^-).[8,9] The reversal in reactivity as compared to that in polar protic solvents is attributed to differences in solvation energies.[1]

$$Ar^. + X^- \rightarrow Ar - X^{.-} \tag{1}$$

The reactions between aryl radicals and nucleophiles, a key step in the $S_{RN}1$ 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 X^- is halide and the solvent DMF, both of the factors would appear to suggest that the reactivity order is expected to be $Cl^- > Br^- > I^-$.

Aryl radicals can be conveniently generated by the reduction of the corresponding diazonium 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 X^-. Since there is some uncertainty in the estimation of k_6, we can use an approximate value of 10^{10} M^{-1} s^{-1} as a reasonable estimate.

$$Ar - N_2^+ + I^- \rightarrow Ar^. + N_2 + \tfrac{1}{2}I_2 \tag{2}$$

$$Ar^. + SH\,(DMF) \rightarrow Ar - H + S^. \tag{3}$$

$$Ar^. + X^- \rightarrow Ar - X^{.-} \tag{4}$$

$$Ar^. + I^- \overset{k_5}{\rightarrow} Ar - I^{.-} \tag{5}$$

$$Ar^. + I_2 \overset{k_6}{\rightarrow} Ar - I + I^. \tag{6}$$

$$Ar - X^{.-} + I_2 \overset{k_7}{\rightarrow} Ar - X + I_2^{.-} \tag{7}$$

Experiments were carried out in which equimolar amounts of $Ar - N_2^+$ (Ar = p-nitrophenyl) and I^- were allowed to react in the presence of an excess of I_2 in DMF. The relative rates of reactions (3) and (6) could then be determined from the mol ratios, $n(Ar - I)/n(Ar - H)$ of the products and $n(DMF)/n(I_2)$ of the reactants, assuming that reaction (5) contributed negligibly to the formation of $Ar - I$ under the reaction conditions. Using a value of 10^{10} M^{-1} s^{-1} for k_6, a value of 6×10^6 M^{-1} s^{-1} was estimated for k_3. Other rate constants could then be estimated using eqn. (8) where X^- is halide reacting in

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

reactions (4) or (5). When X^- was I^-, the conditions were such that reaction (6) did not contribute significantly to the formation of $Ar - I$. For each mol of $Ar - N_2^+$ reacting, one half mol of I_2 is formed but since k_6 and k_7 are diffusion controlled rate constants most of the I_2 is expected to be consumed in (7) since the steady state concentration of $Ar - X^{.-}$ is expected to exceed that of $Ar^.$. That (6) does not interfere with the determination of the relative rate constant for (5) was shown by variable concentration studies in work connected with that published on the reactions of α-naphthyl radical.[11]

Data for reactions carried out in DMF at 22 °C are summarized in Table 1. In the absence of tetraalkylammonium ions the rate constants for the reactions of I^-, Br^- and Cl^- with 4-nitrophenyl radical were estimated to be equal to 5.0×10^9, 5.5×10^8 and 2.8×10^7 M^{-1} s^{-1}, respectively. Of the alkali metal salts used, both KI and KBr are expected to be completely dissociated in DMF[13] while some association of LiCl is to be expected. $LiNO_3$ is more highly associated in DMF than $LiCl$.[14] In the presence of excess Bu_4NNO_3, which would be expected to free any Cl^- associated with 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.[a]
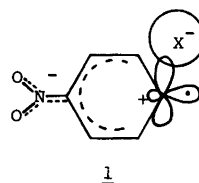
MX(mmol)[b]		R$_4$NX(mmol)[b]		ArH/ArX[c]	k_{rel}[d]
KI	(0.50)	—		0.336	1.000
KI	(0.50)	Et$_4$NBF$_4$	(0.50)	0.366	0.918
KI	(0.50)	Et$_4$NBF$_4$	(1.00)	0.418	0.804
KBr	(0.50)	—		3.19	0.105
KBr	(0.50)	Et$_4$NBF$_4$	(0.25)	3.12	0.108
KBr	(0.50)	Et$_4$NBF$_4$	(0.50)	3.35	0.100
KBr	(0.50)	Et$_4$NBF$_4$	(1.00)	347	0.0968
—		Et$_4$NBr	(0.50)	3.63	0.0926
LiCl	(2.50)	—		12.1	0.00555
LiCl	(2.50)	Bu$_4$NNO$_3$	(1.00)	15.9	0.00423
—		Bu$_4$NI	(1.00)	0.431	0.390

[a] The radical was generated by the reduction of 4-nitrophenyldiazonium ion by iodide ion according to Ref. 11. [b] The salts were dissolved in DMF (10.0 ml) under N$_2$ before adding the diazonium salt (0.05 mmol) in DMF (1.0 ml). [c] The ratio of products was determined by GLC. [d] The 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 Et$_4$N$^+$ 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[15] 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 Bu$_4$N$^+$ 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

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

Halide[a]	$(10^n)_{rel}$[b]	k_{rel}[c]	k_{rel}[d]
Chloride	0.01	0.005	0.011
Bromide	0.063	0.105	
Iodide	1.00	1.00	1.00

[a] Data taken from Table 1. [b] The nucleophilicity constants *n* are from Ref. 15. [c] Value refers to experiments with only alkali metal halides. [d] From experiments on solutions containing Bu$_4$N$^+$ (0.1 M).

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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$-$N$_2^+$ 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$-$N$_2^+$ when I$^-$ is excluded from the reaction mixture. Neither Cl$^-$ nor Br$^-$ are capable of reducing Ar$-$N$_2^+$ 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.[16] The results reported here indicate that the aryl radicals are soft electrophiles reacting most rapidly with polarizable soft nucleophiles.

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