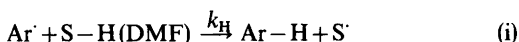


The Selectivity of Aryl Radicals in Reactions with Halide Ions. The Key Step in the S_{RN}I Mechanism

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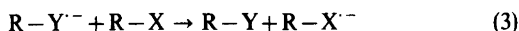
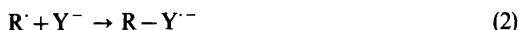
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The relative rate constants for the reactions of *p*-nitrophenyl radical with DMF (i) and halide ions (ii) were determined over a 40 K temperature range.

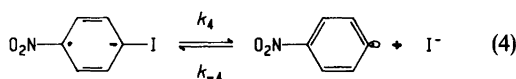


At 273 K the relative reactivity of halide ions in reaction (ii) was observed to be 143 (I[−]), 9.4 (Br[−]) and 1.0 (Cl[−]). Iodide ion was found to be 1.8 times more reactive toward the radical than CBr₄ which is believed to react at a nearly diffusion-controlled rate. The most unexpected feature of the data is the high degree of selectivity for reactions taking place at rates near the diffusion-controlled limit. The activation parameter measurements emphasize the important role of the entropies of activation in determining the rates of very fast reactions. Relative activation energies were observed to be 0 (I[−]), 4.2 (Br[−]) and 5.1 (Cl[−]) for the halide ion-radical reactions leading to expected relative rate constants of 1.2×10^4 (I[−]), 5.25 (Br[−]) and 1.0 (Cl[−]) at 273 K when the differences in activation entropies are neglected. The observed relative reactivities were considerably different.

The S_{RN}I mechanism is a chain process involving propagation steps (1)–(3).¹ The term, S_{RN}I, was applied to the mechanism by Kim and Bunnett who



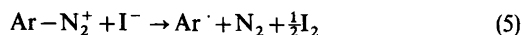
pointed out the analogy with the S_NI mechanism, the intermediates of which have one less electron.² The reaction sequence was first proposed in 1966 for aliphatic systems^{3,4} and a similar mechanism had been proposed to account for phenylation of some carbanions.⁵ The first clearly defined report of reaction (2) where R is aryl appeared in 1969 when Lawless and Hawley⁶ observed that reaction (4), in the forward direction is inhibited by iodide ion



implicating the occurrence of the back reaction. Reaction (4) has recently been studied in both the forward⁷ and reverse⁸ directions and the rate and equilibrium constants have been estimated.

In order to study reaction (2) under conditions where the overall kinetics are not complicated by reactions (1) and (3) it is necessary to fulfill a number of demands. A clean and convenient source of the radical (2) must be available. Reaction (2) must be essentially irreversible under the measurement conditions in order that kinetic measurements refer to the microscopic rate constant for the forward reaction. When the reactions are studied by competition techniques, a well-characterized competing reaction must be available for comparison.

As the source of aryl radicals for reactivity studies, we have chosen the reduction of aryldiazonium ions with iodide ion (5). This reaction and the subsequent



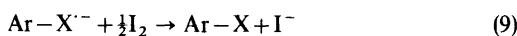
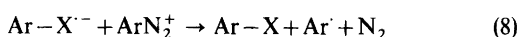
reaction of Ar[·] with iodide ion is one of the early examples of the S_{RN}I reaction in the aromatic series.⁹

The reaction was applied to the generation of α -naphthyl radical and the estimation of the rate constant of the $S_{RN}1$ reaction with thiophenolate ion.¹⁰ A preliminary report of the kinetics of the reactions of 4-nitrophenyl radical with halide ions has recently appeared.⁸ We have recently studied the reactions of 4-nitrophenyl and α -naphthyl generated in reaction (5), with a series of bromomethanes in some detail.¹¹

In order to study the relative reactivities of halide ions in reaction (2), the aryl group must be selected carefully. The cleavage of aryl halide anion radicals is a facile reaction.^{6,12-17} When the aryl group is phenyl, 4-cyanophenyl, α -naphthyl, or 4-benzoylphenyl, cleavage of halide ion (6) is so rapid that it would not be possible to study the corresponding



aryl radical-halide ion reactions as essentially irreversible processes. In fact, halide ions are the most common leaving groups in the $S_{RN}1$ reaction.^{1,2} The cleavage of 4-halonitrobenzene anion radicals takes place at rates low enough, *i.e.* less than 10 s^{-1} ,^{6,7} that reaction conditions can be found where the reactions are essentially irreversible. For the case where the aryl radical is generated in reaction (5) and reacts with halide ion in (7), two very rapid reactions (8) and (9) are available to



immediately oxidize the anion radical. The oxidation potentials of the 4-halonitrobenzene anion radicals are more negative than 1 V *vs.* S.C.E. while reduction of ArN_2^+ occur at about 0 V¹⁸ and of I_2 at about +0.5 V. Thus, both (8) and (9) are expected to be diffusion controlled.

The reaction of the aryl radical with DMF (10) is a convenient competitive reaction to compare relative rates of (7) with.^{8,10} Reaction (10) is rapid



enough so that significant amounts of $\text{Ar}-\text{H}$ are formed in competition with $\text{Ar}-\text{X}$ so that the product distribution can readily be determined by GLC.

In this paper we report the details of the reactions of 4-nitrophenyl radical with iodide, bromide and chloride in DMF in the presence of tetrabutylammonium fluoroborate.

RESULTS

The analysis procedure involved GLC determinations of the composition of the reaction mixtures obtained after generation of 4-nitrophenyl radical by reduction of the corresponding diazonium ion in DMF in the presence of the appropriate halide ion.^{8,10,11} Relative rate constants for reactions (10) and (7) were calculated using eqn. (11) where the mol ratio of reactants ($n_{\text{X}}/n_{\text{DMF}}$) remained unchanged

$$k_{\text{H}}/k_{\text{X}} = (A_{\text{H}}/A_{\text{X}})(r_{\text{H}}/r_{\text{X}})(n_{\text{X}}/n_{\text{DMF}}) \quad (11)$$

Table 1. Competition kinetic data for the reactions of 4-nitrophenyl radical with halide ions and DMF.^a

X^-	$n_{\text{DMF}}/n_{\text{X}}^b$	$T/^{\circ}\text{C}$	$10^3(k_{\text{H}}/k_{\text{X}})_{\text{obs}}^c$	$10^3(k_{\text{H}}/k_{\text{X}})_{\text{corr.}}^d$
I^-	545	0	0.853	0.865
I^-	545	22.0	1.40	1.35
I^-	545	39.9	1.82	1.86
Br^-	272	0	13.0	13.1
Br^-	272	21.9	11.7	11.6
Br^-	272	39.8	10.6	10.7
Cl^-	54.5	0	122	122
Cl^-	54.5	21.6	94.3	94.9
Cl^-	54.5	39.8	79.3	79.0

^a The radicals were generated by the reduction of $\text{ArN}_2^+ \text{BF}_4^-$ with I^- in DMF. ^b The mol ratio of DMF and the halide ion. ^c The observed rate constant ratio. ^d The rate constant ratio calculated from the Arrhenius correlation line.

Table 2. Differential activation parameters for the reactions of 4-nitrophenyl radicals with DMF and halide ions.^a

X ⁻	ΔE_a^b /(kcal/mol)	$\Delta\Delta S_{273}^b$ /(cal/K mol)
I ⁻	3.3	-2.0
Br ⁻	-0.87	-11.8
Cl ⁻	-1.84	-10.9

^aRate constant data from Table 1. ^bThe activation parameters are those of DMF minus those for the halide ion reactions.

during the reaction and the ratio of GLC peak areas (*A*) was determined in each experiment. The sensitivity factors *r* were determined by measurements on mixtures of known composition. Measurements were carried out at three different temperatures over a 40 K range for the reactions of I⁻, Br⁻ and Cl⁻ with 4-nitrophenyl radical. The data are summarized in Table 1.

Differential activation energies (ΔE_a) were obtained by Arrhenius correlations. The last column in Table 1 gives k_H/k_X obtained from the correlation. Only one value, that for I⁻ at 22 °C, differed from the experimental value by more than 2 %. In general, the relative rate constants obtained from the correlation were within 1 % of the experimental value. The ΔE_a values along with the differential entropies of activation ($\Delta\Delta S_{273}^\ddagger$) obtained using eqn. (12)

$$\Delta\Delta S_{273}^\ddagger = R \ln (k_H/k_X) + \Delta E_a/T \quad (12)$$

are listed in Table 2. Rate constant ratios, ΔE_a and $\Delta\Delta S_{273}^\ddagger$ for the reactions of Br⁻, Cl⁻ and CBr₄¹¹ taking the reaction of the radical with I⁻ as the reference are summarized in Table 3.

Table 3. Relative rate constants and differential activation parameters for the reactions of 4-nitrophenyl radical with halide ions and carbon tetrabromide.^a

Reactant	k_I/k_X	$\Delta E_{a(I-X)}$ /(kcal/mol)	$\Delta\Delta S_{273}$ /(cal K ⁻¹ mol ⁻¹)
I ⁻	1.0	0	0
Br ⁻	15.2	4.2	9.8
Cl ⁻	143	5.1	8.9
CBr ₄	1.8	1.3	4.0

^aAll reactions referred to those with iodide ion, data for CBr₄ are from Ref. 11.

DISCUSSION

The relative rate constants reported previously⁸ for the reactions of 4-nitrophenyl radical with halide ions at 22 °C in DMF were measured in the presence of alkali metal counter ions. The values, 1.00 (I⁻), 0.11 (Br⁻) and 0.005 (Cl⁻) are in accord with those found in this study in which Bu₄N⁺ was the only counter ion present; i.e. 1.00 (I⁻), 0.12 (Br⁻) and 0.014 (Cl⁻) with the exception of the latter which is somewhat greater than reported previously.*

The data gathered in Table 3 for the reactions of 4-nitrophenyl radical at 0 °C are instructive. The activation energies for the reactions with Br⁻ and Cl⁻ are considerably greater than that for I⁻, 4.2 and 5.1 kcal/mol, respectively. Neglecting the entropies of activation the ΔE_a data lead to the prediction of a much larger range of relative rate constants than was observed, 1.2×10^4 (I⁻), 5.25 (Br⁻) and 1.0 (Cl⁻). The reason for this is that the entropies of activation are very much more positive when the nucleophile is either Br⁻ or Cl⁻. Data are also included for the bromide abstraction from CBr₄¹¹ since this reaction is expected to be near the diffusion controlled limit in analogy to the corresponding reaction of phenyl radical.¹⁹

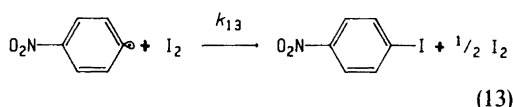
The data in Table 4 are gathered in order to give estimates of the absolute rate constants and activation parameters for the reactions of 4-nitrophenyl radical in DMF at 22 °C, a temperature common to all of the data reported. As a reference point, the most rapid reaction that has been studied, that with I₂ (13)⁷ was assumed to have an encounter-con-

*The last entry in Table 1 of Ref. 8 is apparently in error. Under comparable conditions,⁷ k_{rel} has been observed to be close to unity which is in accord with the results of this study and also gives a better comparison with the reaction in the presence of potassium ion.

Table 4. Estimated bimolecular rate constants and activation parameters for the reactions of 4-nitrophenyl radical.^a

Reactant	Data from	$10^9 k/M^{-1}s^{-1}$	$E_a/kcal\ mol^{-1}$	$\Delta S_{295}/cal\ K^{-1}\ mol^{-1}$
I ₂	b, c	5.8	2.4	-7.7
I ⁻	d, c	2.5	2.4	-9.4
CBr ₄	e	1.4	3.7	-6.1
Br ⁻	d	0.16	6.6	-0.6
Cl ⁻	d	0.018	7.5	-1.9
DMF	b, d	0.0035	5.7	-11.2

^a For reactions in DMF. The rate constant for the reaction between the radical and iodine was calculated from the Smoluchowski equation and all others are from values relative to that rate constant. ^b Ref. 7. ^c Ref. 21. ^d This work.



trolled rate constant. The magnitude of k_{13} was estimated from the Smoluchowski equation (14)²⁰ where r (the sum of the effective radii) was taken to be 5 Å and the mutual diffusion coefficient D_{AB} twice

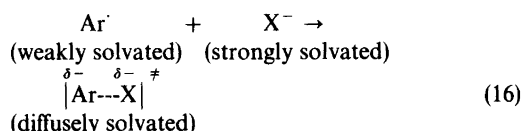
$$k_{en} = 4\pi\kappa r D_{AB} N / 1000 \quad (14)$$

the average experimental value²¹ for a number of aromatic compounds in DMF. This resulted in a value of $5.8 \times 10^9\ M^{-1}\ s^{-1}$ for k_{13} . The activation energy was taken to be that for diffusion in DMF and here again an average experimental value,²¹ 2.4 kcal/mol was assumed. The entropy of activation ΔS_{295}^\ddagger was then calculated using eqn. (15). Since the differential activation energy for reaction (13)

$$\Delta S_f^\ddagger = R(\ln k - \ln ek/h - \ln T) + E_a/T \quad (15)$$

has not been determined, E_a for the reaction with iodide ion, reverse reaction (4), was also taken to be 2.4 kcal/mol. The latter seems reasonable in view of the fact that the rate constants for the two reactions only differ by a factor of about 2. All other E_a values could then be assigned from the differential values determined in this study or in the case of CBr₄, previously.¹¹

The origin of the large negative apparent entropies of the activation for diffusion-controlled reactions remains uncertain.²¹ The significantly more positive ΔS^\ddagger for the reactions of Br⁻ and Cl⁻ most likely arises from the desolvation of the halide ions on going from reactants to transition state (16). The entropy change for reaction (17) can be predicted to be strongly positive. The standard entropies of



Br⁻ and Cl⁻ in DMF have been reported to be -43.3 and -46.7 cal/K mol.²² The value of ΔS for the formation of nitrobenzene anion radical has been observed to be much less negative, -11.7 cal/K mol at 273 K.²³ Thus, assuming that ΔS for 4-nitrophenyl radical in DMF is the same as that of nitrobenzene, ΔS for reaction (17) can be estimated to be +32 and +35 cal/K mol when X⁻ is bromide and chloride, respectively.

We now have adequate data to use in the consideration of equilibrium (18) in some detail. The pertinent data are gathered in Table 5. The values

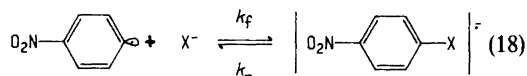


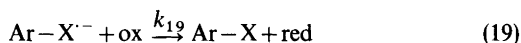
Table 5. Rate and equilibrium constants for the reactions of 4-nitrophenyl radical with halide ions in DMF.^a

X	$k_f/M^{-1}s^{-1}\ ^b$	$k_r/s^{-1}\ ^c$	K/M^{-1}
I	2.0×10^9	6.7	3×10^8
Br	1.3×10^8	1.4×10^{-3}	9×10^{10}
Cl	1.4×10^7	1×10^{-6}	1×10^{13}

^a Refer to equilibrium (18). ^b Values from Table 4 referring to 295 K. ^c Values for I and Br from Ref. 7 and that for Cl estimated from the relative rates of cleavage of haloanthracene anion radicals ($k_{Br}/k_{Cl} = 2000$)²⁴ and of halobenzophenones ($k_{Br}/k_{Cl} = 1000$).¹⁷ The rate constants refer to 298 K.

of the rate constants in the forward direction (k_f) are from Table 4. The rate constants referring to the reverse direction (k_r) have been reported in DMF for the 4-bromo and 4-iodonitrobenzene anion radicals.⁷ 4-Chloronitrobenzene anion radical is stable in DMF. However, two series of reactions have recently been investigated which have bearing on the reaction in question. The relative rate constants for the cleavage of bromide and chloride (k_{Br}/k_{Cl}) were observed to be of the order of 2000 and 1000, during the cleavage of 9-haloanthracene¹⁶ and 4-halobenzophenone¹⁷ anion radicals, respectively. Thus, we can estimate k_r when $X=Cl$ to be of the order of 10^{-6} s^{-1} at 298 K. Equilibrium constants estimated for reaction (18) are very large ranging from 3×10^8 to 10^{13} .

This same type of analysis is not possible for the reactions of the halide ions with radicals such as phenyl, naphthyl, *p*-cyanophenyl or *p*-methoxyphenyl since the corresponding anion radical cleavage reactions (6) are too rapid. The kinetics in such cases are then complicated by competition of (6) with (19) and the rate laws are expected to be of the form of (20), where ox and red refer to oxidation



$$\text{rate} = k_{-6} k_{20} [\text{Ar}^{\cdot-}] [\text{X}^{\cdot-}] / (k_6 + k_{20} [\text{ox}]) \quad (20)$$

states of the oxidant in (19). On the other hand, if one goes to better nucleophiles, and poorer leaving groups, little is to be gained since the reactions will surely be at the diffusion-controlled limit. Thus, we regard the 4-nitrophenyl radical-halide ion reaction and the reverse cleavage as the optimum system to study in order to gain detailed information about the key step in the $S_{RN}1$ mechanism. The results reported here can be used to predict parameters for related systems.

EXPERIMENTAL

The experimental procedures and the analysis of the data were the same as those recently described in detail.¹¹

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