

Ion Radical Cleavage Reactions. II. Kinetics and Equilibria of the Cleavage of Halide Ion from 4-Halonitrobenzene Anion Radicals

VERNON D. PARKER

Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

The kinetics of the unimolecular cleavage reactions of 4-halonitrobenzene anion radicals in *N,N*-dimethylformamide (DMF) and acetonitrile were investigated as a function of temperature and supporting electrolyte. Rate constants ranging from 1 to 8 s⁻¹ with activation energies in the range 17–20 kcal/mol with small activation entropies were observed for the reactions of 4-iodonitrobenzene anion radical. A small temperature dependent kinetic isotope effect was observed in acetonitrile and deuterated solvent. The rate constant in the presence of Bu₄N⁺ was observed to be of the order of 25 % greater than when Me₄N⁺ was the supporting electrolyte cation. The decomposition of 3-iodonitrobenzene anion radical was slower by a factor of 8 but the activation parameters were similar. The activation energy for the decomposition of 4-bromonitrobenzene anion radical was found to be 20.9 kcal/mol and the rate constant lower by a factor of 6,000 as compared to the iodo derivative. The rate constant for the reaction of iodide ion with 4-nitrophenyl radical was estimated to be equal to 5 × 10⁹ M⁻¹ s⁻¹ and the rate constant for the cleavage of iodide from 4-iodonitrobenzene anion radical was found to be equal to 6.7 s⁻¹ under comparable conditions yielding an equilibrium constant of 1.3 × 10⁻⁹ M⁻¹.

In the previous paper in this series, the activation parameters for the cleavage of halide ion from 9-halo- or 9,10-dihaloanthracene anion radicals were found to be strongly dependent upon whether bromide or chloride was the leaving group.¹ For a given halide ion cleavage, the activation energy was the same for mono- or disubstituted anion radicals. The greatest difference between reactions involving chloro- and bromo-substituted anion radicals was that the activation entropies were about 21 e.u.

more negative for the latter. It was proposed that the large differences in activation entropies were due to differences in the degree of bond cleavage in the transition states of the reactions.

In view of the sensitivity of the activation parameters to structure in the haloanthracene anion radical reactions, a reinvestigation of the reactions of halonitrobenzene anion radical reactions was carried out. Rate constants for some of the reactions have previously been reported.² However, no activation parameters were determined and the kinetics were described in terms of pseudo first order rate constants for the abstraction of hydrogen by the nitrophenyl radicals.² Since the reactions of 4-iodonitrobenzene anion radical were observed to be inhibited by iodide ion, the possibility of obtaining data for the reverse reaction, that of iodide ion with the radical was evident.

RESULTS

Kinetic measurements. Rate constants were measured using derivative cyclic voltammetry.^{3,4} The method involves measuring $v_{1/2}$, defined as the voltage sweep rate necessary for the ratio of the derivative peaks on the backward and forward scans of a cyclic voltammogram (R'_1) to equal 0.500.⁵ For the first order reaction following charge transfer, the EC mechanism, the rate constant can be calculated from $v_{1/2}$ using eqn. (1). The method used to find $v_{1/2}$ was to obtain v for three values of R'_1 close to 0.500 and then apply the linear eqn. (2).⁶

$$k = 906.2 v_{1/2} / T \quad (1)$$

$$\ln R'_1 = m \ln(1/v) + c \quad (2)$$

Table 1. Kinetic data for the unimolecular decomposition of 4-iodonitrobenzene anion radical in DMF.^a

$t/^\circ\text{C}$	$v_{1/2}^b/V\text{ s}^{-1}$	k/s^{-1}
Bu₄NBF₄		
20.0	1.50	4.64
32.8	4.60	13.6
42.8	13.4	38.4
61.6	68.5	186
Me₄NBF₄		
21.5	1.22	3.75
32.2	3.54	10.5
41.4	8.40	24.2
52.6	22.0	61.2
Bu₄NI		
22.3	0.24	0.74
34.5	1.05	3.09
45.4	3.05	8.68
59.8	11.2	30.5

^a Measurements at a mercury electrode with a substrate concentration of 1.0 mM and supporting electrolyte concentration of 0.1 M. ^b The voltage sweep rate at which the ratio of the derivative peaks on the backward and forward scans of a cyclic voltammogram equals 0.500.

The temperature was held constant at ± 0.5 K during the time of measurement by having the voltammetric cell immersed in water contained in a Dewar flask. The temperature was measured using a Jenway Model 1002 digital thermometer to a precision of ± 0.1 K.

Kinetics of the decomposition of 4-iodonitrobenzene anion radical in DMF. Rate constants measured over a temperature range of ~ 40 K in the presence of Bu₄NBF₄, Me₄NBF₄ and Bu₄NI are summarized in Table 1. A small decrease in rate constant was observed in going from Bu₄NBF₄ to Me₄NBF₄ and as expected from previous work² a much larger decrease was observed when Bu₄NI was the supporting electrolyte. In all three cases Arrhenius plots were very good with correlation coefficients greater than 0.999.

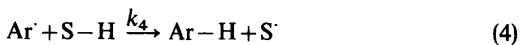
A series of experiments were conducted at 22.3 °C in which the concentration of Bu₄NI was varied from 0 to 0.07 M in solutions held at constant ionic strength by the appropriate concentration of Bu₄NBF₄. The data for these experiments are summarized in Table 2. The reversible reaction (3)

Table 2. Kinetic data for the unimolecular decomposition of 4-iodonitrobenzene anion radical in DMF containing different concentrations of iodide ion.^a

[Bu ₄ NBF ₄]/M	[Bu ₄ NI]/M	$v_{1/2}/V\text{ s}^{-1}$	k/s^{-1}
0.10	0	1.88	5.77
0.09	0.01	1.21	3.71
0.08	0.02	0.83	2.54
0.06	0.04	0.53	1.62
0.03	0.07	0.33	1.01

^a For conditions and definitions see Table 1. The temperature was 22.3 °C.

followed by abstraction of hydrogen atoms from the solvent (4) gives rise to rate law (5) upon application of the steady state assumption on Ar[•].



$$\text{Rate} = k_4 k_3 [\text{Ar-X}^{\cdot-}] [\text{S-H}] / (k_{-3} [\text{X}^-] + k_4 [\text{S-H}]) \quad (5)$$

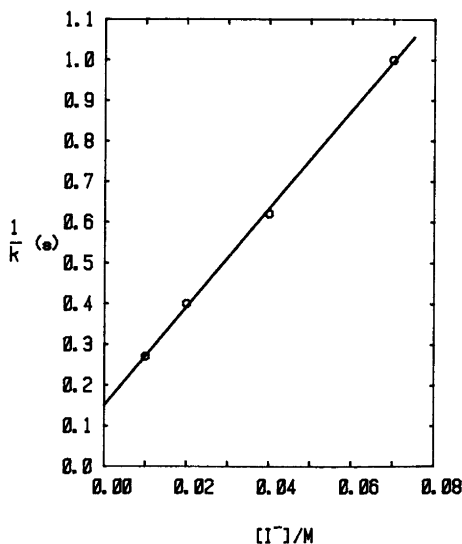


Fig. 1. Influence of iodide ion concentration on the rate constant observed for the cleavage of 4-iodonitrobenzene anion radical in DMF at 22.3 °C.

Table 3. Kinetic data for the unimolecular decomposition of 4-iodonitrobenzene anion radical in acetonitrile.^a

<i>t</i> /°C	$v_{1/2}/V s^{-1}$	<i>k</i> /s ⁻¹
Bu ₄ NBF ₄ ; CH ₃ CN		
18.2	0.170	0.529
28.8	0.580	1.74
38.3	1.79	5.21
49.2	4.70	13.2
Me ₄ NBF ₄ ; CH ₃ CN		
25.5	0.345	1.05
37.0	1.26	3.68
47.9	3.60	10.2
Me ₄ NBF ₄ ; CD ₃ CN		
36.1	0.87	2.55
47.2	2.10	5.94
59.1	5.60	15.3
12.5 ^b	0.082	0.26
23.3 ^b	0.291	0.889
36.1 ^b	0.890	2.60
47.2 ^b	2.06	5.96

^aFor conditions and definitions see Table 1.

^bMeasurements on a solution prepared independent of one used in the previous entries in CD₃CN.

Under conditions where [X⁻] and [S-H] are in excess and constant the observed rate constant (*k*_{obs}) is given by (6) and the inverted form (7) suggests a linear relationship between 1/*k*_{obs} and

$$k_{\text{obs}} = k_4 k_3 / (k_{-3} [X^-] + k_4) \quad k_4 = k_4 [S-H] \quad (6)$$

$$1/k_{\text{obs}} = [X^-] / k_4 K_3 + 1/k_3 \quad (7)$$

[X⁻] which upon extrapolation to [X⁻] equal zero gives 1/*k*₃. Indeed, linear regression analysis of the data in Table 2 results in a slope of 12.1, an intercept equal to 0.15, and a correlation coefficient of 0.9996. The relationship is demonstrated in Fig. 1. From the intercept, the value of *k*₃ was determined to be equal to 6.7 s⁻¹ at 22.3 °C.

A comparable set of reactions (Table 3), with the exception of those involving Bu₄NI, were carried out with acetonitrile as solvent. Once again the rate constants observed in the presence of Me₄NBF₄ were somewhat lower than those when the supporting electrolyte was Bu₄NBF₄. In CD₃CN in the presence of Me₄NBF₄ the rate constants were

Table 4. Kinetic data for the unimolecular decomposition of 3-iodonitrobenzene anion radical in DMF.^a

<i>t</i> /°C	$v_{1/2}/V s^{-1}$	<i>k</i> /s ⁻¹
26.9	0.350	1.057
39.8	1.47	4.26
50.3	3.70	10.4
64.4	12.0	32.2

^aThe supporting electrolyte was Bu₄NBF₄ (0.1 M). For conditions and definitions see Table 1.

lower than when the solvent was CH₃CN indicating a deuterium kinetic isotope effect, the magnitude of which is temperature dependent. Arrhenius plots were linear with correlation coefficients greater than 0.999.

Kinetics of the decomposition of the anion radicals of 3-iodo- and 4-bromonitrobenzene. The rate of decomposition of 3-iodonitrobenzene anion radical in DMF containing Bu₄NBF₄ was of a magnitude suitable for study in the same temperature range as used for the 4-iodo derivative. The data are summarized in Table 4. On the other hand, no reaction could be detected by cyclic voltammetry during the reduction of 4-bromonitrobenzene in the same electrolyte system at 20 °C. The rate constant for the cleavage of bromide ion could be determined at temperatures ranging from 55 to 82 °C. The data, summarized in Table 5, point out that it can be of value to go to higher temperatures, which is seldom done, during electrode kinetic studies. Linear Arrhenius plots were observed for the data in both Tables 4 and 5.

Activation parameters for the halonitrobenzene anion radical cleavage reactions. Activation energies (*E*_a) and rate constants at 298 K (*k*₂₉₈) were ob-

Table 5. Kinetic data for the unimolecular decomposition of 4-bromonitrobenzene anion radical in DMF.^a

<i>t</i> /°C	$v_{1/2}/V s^{-1}$	<i>k</i> /s ⁻¹
55.6	0.127	0.35
65.7	0.380	1.02
74.8	0.80	2.08
81.8	1.50	3.83

^aThe supporting electrolyte was Bu₄NBF₄ (0.1 M). For conditions and definitions see Table 1.

Table 6. Activation parameters for the decomposition reactions of halonitrobenzene anion radicals in aprotic solvents.^a

Solvent	Electrolyte	E_a /(kcal/mol)	ΔS_{298}^\ddagger ^b	k_{298}/s^{-1}
DMF	Bu ₄ NBF ₄	17.5	2.1	7.17
DMF	Bu ₄ NI	19.3	4.3	1.05
DMF	Me ₄ NBF ₄	17.1	0.2	5.31
CH ₃ CN	Bu ₄ NBF ₄	19.6	5.5	1.17
CH ₃ CN	Me ₄ NBF ₄	19.3	4.2	1.01
DMF ^c	Bu ₄ NBF ₄	18.2	0.4	0.92
DMF ^d	Bu ₄ NBF ₄	20.9	1.0	0.0014

^a Calculated from data in Tables 1–5, all but the last two entries refer to reactions of 4-iodonitrobenzene anion radical.

^b Entropy of activation in units of cal/K mol. ^c For the reaction of 3-iodonitrobenzene anion radical. ^d For the reaction of 4-bromonitrobenzene anion radical.

tained from linear regression analysis of $\log k$ vs. T^{-1} data. These, along with entropies of activation at 298 K (ΔS_{298}^\ddagger) are summarized for all of the reactions in Table 6. The ΔS_{298}^\ddagger were calculated from eqn. (8) where k/h is Boltzmann's constant

$$\Delta S_T^\ddagger = R(\ln k_T - \ln(ek/h) - \ln T) + E_a/T \quad (8)$$

divided by Planck's constant.⁷

Kinetics of the reaction of 4-nitrophenyl radical with iodide ion. In a previous section it was shown that manipulation of the data for the cleavage of 4-iodonitrobenzene anion radical in the presence of varying concentrations of iodide ion resulted in the rate constant for the cleavage reaction (3) and the product k_4K_3 , where k_4 is the rate constant for the hydrogen abstraction reaction (4). In order to achieve further kinetic detail, it is necessary to use independent kinetic techniques. A convenient method for the study of aryl radical reactions is to generate the radicals by reduction of the corresponding diazonium ions with iodide ion (eqn. 9).⁸



Since the reaction of aryl radicals with iodine (10) is diffusion controlled,⁹ this provides a reference to calculate rate constants for the reaction of aryl radicals with iodide ion (11) and the hydrogen abstraction reaction (4).



The data in Table 7 serve to provide estimates of both k_{11} ($=k_3$ when $X^- = \text{I}^-$) and k_4 . The product mixtures obtained after generating the 4-nitrophenyl radical according to (9) were analyzed by GLC. The value of $k(\text{I}_2)$ ($=k_{10}$) was taken to be equal to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and the value of k_{DMF} ($=k_4$) was calculated from eqn. (12) and k_{11} from (13). The ratios refer to mol ratios of reactants and products.

$$k_{\text{DMF}} = (\text{Ar-H}/\text{Ar-I})(\text{I}_2/\text{DMF})k(\text{I}_2) \quad (12)$$

$$k_{11} = (\text{Ar-I}/\text{Ar-H})(\text{DMF}/(\text{I}^-))k_{\text{DMF}} \quad (13)$$

Table 7. Reactions of 4-nitrophenyl radical generated by reduction of the diazonium ion in DMF.^a

I ₂ /mmol	Bu ₄ NI/mmol	ArI/ArH ^b	k_{DMF}^c	k_1^c
0.14	0.05	1.64	6.0×10^6	—
—	0.50	2.94	—	5.0×10^9

^a 4-Nitrophenyldiazonium tetrafluorborate (0.05 mmol) in DMF (1.0 ml) was added to solutions of the other reactants in DMF (10.0 ml) at 22°C. ^b The ratio of products determined by GLC, Ar refers to 4-nitrophenyl. ^c Second order rate constants in $\text{M}^{-1} \text{ s}^{-1}$ calculated from the ratios of products and reactants assuming that the reaction of 4-nitrophenyl radical with I₂ is diffusion controlled with a rate constant of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

DISCUSSION

The reactions of halonitrobenzene anion radicals are somewhat more complex than the cleavage reactions of haloanthracene anion radicals.¹ The complexity is evident from the fact that the 4-iodonitrobenzene anion radical is longer lived in the presence of iodide ion due to the reversibility of the cleavage reaction (3). That the hydrogen atom abstraction step also participates in determining the rate is indicated by the observation of the deuterium kinetic isotope effect in acetonitrile and acetonitrile-*d*₃. Thus, there is a little more uncertainty as to the origin of the activation parameters. On the other hand, a comparison of the first two sets of data in Table 6, the first where the supporting electrolyte was Bu₄NBF₄ and the second with Bu₄NI, shows that it is only the rate of the reaction that is appreciably affected by the reverse reaction. Also, the data in Table 2 resulted in an extrapolated value of 6.7 s⁻¹ for the value of *k*₃ at zero iodide concentration. The measured value with only Bu₄NBF₄ present was 5.7 s⁻¹. The latter indicates that the inhibitory effect of iodide ion, generated during the cleavage reaction, is small. Thus, the activation parameters given in Table 6 can be taken, with some reservations, to be a reflection of the energetics of forward reaction (3).

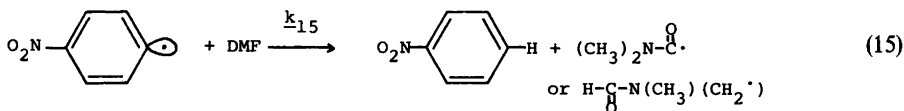
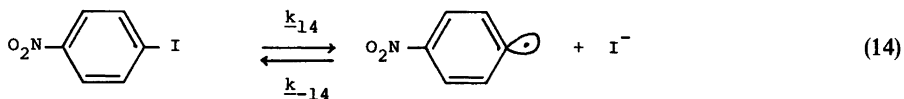
The first and last data entries in Table 6 give a comparison of 4-iodo and 4-bromo as leaving groups in reaction (3). The values of Δ*S*₂₉₈[‡] are very nearly the same at 2.1 and 1.0 cal/deg mol. The activation energy is 3.4 kcal/mol greater for 4-bromonitrobenzene anion radical which results in *k*₂₉₈ being about 6,000 times as great for the 4-iodo derivative. This is qualitatively the same trend that was found with the haloanthracene anion radicals where the bromo derivatives were observed to cleave about 2000 times as fast as the corresponding chloro-substituted anion radicals.¹

With the exception of the reactions carried out in CD₃CN, Δ*S*₂₉₈[‡] was small and positive. A reasonable interpretation of this is that the charge in the anion radicals is to a large extent localized

on the nitro group which results in appreciable ordering of the solvent in the vicinity of that portion of the anion radical. In the transition state the charge is being spread over the structure and onto the halogen atom which contributes to a less ordered solvent structure and an increase in entropy. The situation was very different with the haloanthracene anion radicals in which case the magnitude of Δ*S*₂₉₈[‡] was strongly dependent upon the identity of the halogen atom. The differences observed in the two systems must be a consequence of the very strong tendency of the nitro group to attract the charge in the anion radical. Thus, the nitro group bears the bulk of the charge irregardless of the nature or position of the halogen substituent. On the other hand, the distribution of charge in the anthracene derivatives is apparently much more susceptible to changes with different substituents.

The apparent *k*_H/*k*_D for the reaction of 4-iodonitrobenzene anion radical in CH₃CN and CD₃CN was observed to be equal to 1.90 at about 47 °C, 1.42 at about 36 °C and 0.99 at 23.3 °C. The temperatures for the first two values differed slightly while the third was obtained by extrapolation of the CH₃CN data. The feature of interest is that the isotope effect is temperature dependent and small. The rate constants measured at 12.5 and 23.3 °C in CD₃CN are within experimental error of the Arrhenius correlation line of the CH₃CN data indicating that *k*_H/*k*_D is unity in that temperature range. Thus, in CH₃CN and at lower temperatures in CD₃CN, reaction (4) does not contribute to controlling the rate and the observed rate constant can be equated to *k*₃. On the other hand, in CD₃CN at higher temperatures the apparent rate constant is equal to *k*₃*k*₄/(*k*₋₃[I⁻] + *k*₄). Apparently, the latter situation arises because of a lower *E*_a for reaction (4). Because it is not possible to find conditions where the apparent rate is only a reflection of reaction (4), the intrinsic *k*_H/*k*_D for that reaction could not be obtained.

The homogeneous kinetic studies of the reactions of 4-nitrophenyl radical with iodide ion and DMF along with the extrapolated value for the rate



constant for the cleavage reaction (7) and the slope from that relationship allow a complete assignment of rate constants for the reactions (14) and (15). However, there is some discrepancy between data from the two types of experiments. From the relationship described by eqn. (7) we obtain k_{14} equal to 6.7 s^{-1} and $K_{14} = 1/12.1[\text{DMF}]k_{15}$. Making the appropriate substitutions we then arrive at $k_{-14}/k_{15} = 1.05 \times 10^3$. The value obtained directly from the reactions of 4-nitrophenyl radical with DMF and iodide ion in competition experiments was 8.4×10^2 (Table 7). Using the electrochemical data along with the rate constant obtained for the reaction between the radical and DMF results in a value of $1.1 \times 10^{-9} \text{ M}$ for K_{14} . Another approximation that must be kept in mind with regard to the evaluation of K_{14} is that the diffusion controlled rate constant for the reaction between the radical and iodine was used as a standard and it was estimated to be equal to $10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

In terms of the mechanism of the reaction, the uncertainties involved in the estimation of K_{14} are not very serious. The way in which the 4-nitrophenyl radical partitions between reacting with iodide and the solvent remains uncertain by a factor of 0.8 which is not such a serious error with reactions approaching the diffusion controlled limit.

It is apparent from this discussion that Lawless and Hawley's description of the kinetics of the cleavage reactions as pseudo first order hydrogen abstraction reactions² was rather inappropriate. The cleavage reaction plays the most important role in the kinetics. Under conditions where iodide ion is not added, $k_{15}[\text{DMF}] \gg k_{-14}[\text{I}^-]$, and k_{14} plays a predominate role in the kinetics. The other reactions were not investigated in the same depth as that for 4-iodonitrobenzene anion radical but it is reasonable to expect the same situation to prevail in those cases.

EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures as well as solvent and electrolyte purification were the same as recently described.¹⁰

4-Iodonitrobenzene and 4-bromonitrobenzene were prepared by nitration of the corresponding halobenzene. 3-Iodobenzene was previously prepared by Lines.¹¹ After recrystallization, GLC analysis indicated >99 % purity in all cases.

The diazonium salt was prepared by a standard procedure.¹² The reactions of the 4-nitrophenyl radical were initiated by injecting a solution of the diazonium salt (0.05 mmol in 1.0 ml of DMF) into the solution containing iodide ion or iodine and iodide ion in DMF (10.0 ml) while rapidly stirring using a nitrogen bubbler. The solutions were diluted with water (10 ml) containing $\text{Na}_2\text{S}_2\text{O}_3$ to destroy any I_2 and then extracted with light petroleum (10 ml). GLC analyses were carried out using a Perkin Elmer 2920 B gas chromatograph coupled to a Hewlett Packard 3380 S integrator.

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