

Ion Radical Cleavage Reactions. I. The Kinetics and Activation Parameters for the Cleavage of Halide Ion from Haloanthracene Anion Radicals

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The kinetics of the unimolecular decomposition reactions of 9-halo- and 9,10-dihaloanthracene anion radicals were studied as a function of temperature. Arrhenius activation energies were found to be nearly independent of whether mono- or disubstituted anion radicals were undergoing decomposition. Activation energies of 15.2 kcal/mol were found for the 9-chloro and 9,10-dichloro substituted anion radical while a value of 4.0 kcal/mol was observed for the corresponding bromo substituted ions. However, the mono substituted anion radicals were observed to be of the order of 7.5 times more reactive than the corresponding 9,10-disubstituted ions while the bromo substituted anion radicals react 2000 times faster than the chloro derivatives. The entropy of activation decreased in the order 9-chloro > 9,10-dichloro > 9-bromo > 9,10-dibromo with the observed values of -0.1 , -4.1 , -22 and -26 cal/(K mol), respectively. The origin of the entropy of activation differences are proposed to lie primarily in the differences in the degree of bond cleavage in the transition states for the cleavage reactions. The rate of cleavage of 9,10-dichloroanthracene anion radical was observed to be independent of whether the solvent was *N,N*-dimethylformamide or acetonitrile or whether Bu_4N^+ or Me_4N^+ was the counter ion. The rate of the reaction was found to be only slightly dependent upon the salt concentration. Activation parameters measured under all experimental conditions were essentially identical.

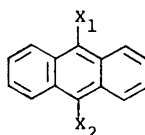
Although a large volume of literature exists on the cleavage reactions of aryl halide anion radicals,^{1–5} no information is available on the activation parameters for the reactions. The reactions are con-

sidered to be simple EC processes (eqns. 1 and 2) which represent the ideal case for detailed kinetic



studies since the observed rate constants should be equal to the microscopic rate constant for reaction (2).

As a starting point of a detailed investigation of this class of reactive intermediate reactions, it was decided to make a comparison of the reactivity of the anion radicals of the haloanthracenes (1). The rate constants for the cleavage of two of the anion radicals, those from *1-a* and *1-c* have been reported.¹



	X ₁	X ₂
<i>1-a</i>	Cl	H
<i>1-b</i>	Cl	Cl
<i>1-c</i>	Br	H
<i>1-d</i>	Br	Br

RESULTS

Kinetic measurements. Rate constants for the decompositions of the anion radicals were measured

Table 1. Derivative cyclic voltammetry kinetic study of the unimolecular cleavage reaction of 9-chloroanthracene anion radical in *N,N*-dimethylformamide.

$v/V s^{-1}$	$T/^{\circ}C$	$(R)_i^a$	$(k/s)^b$
10	13.0	0.479	36.4
20	13.0	0.630	41.5
40	13.0	0.783	38.9
10	22.0	0.294	90.2
20	22.0	0.402	99.4
40	22.0	0.570	92.2
70	22.0	0.692	100.1
100	22.0	0.770	99.4
10	29.0	0.234	149.8
20	29.0	0.307	157.7
40	29.0	0.424	168.3
70	29.0	0.559	161.9
100	29.0	0.654	159.3
20	38.0	0.223	336.0
40	38.0	0.287	343.2
70	38.0	0.378	355.4
100	38.0	0.458	336.0

^aThe ratio of the peaks of the first derivative of the reverse and forward scans of a cyclic voltammogram.
^bRate constant obtained from a theoretical working curve.

using derivative cyclic voltammetry.^{6,7} The data in Table 1 obtained for the reaction of *1-a* anion radical in *N,N*-dimethylformamide (DMF) serve to illustrate the data. In general, rate constants measured over the sweep rate range of 10 to 100 Vs^{-1} had standard deviations of about 5% or less. The excellent fit of the experimental to theoretical data for the simple EC mechanism (eqns. 1 and 2) strongly support the previous mechanism assignments.¹⁻⁵ A similar series of measurements on the reactions of the anion radicals of *1-b* and *1-d*

Table 2. Rate constants for the unimolecular decomposition of 9,10-dichloroanthracene anion radical in *N,N*-dimethylformamide.

$T/^{\circ}C$	$(k/s^{-1})^a$
13.0	5.01(0.10)
25.9	17.8 (1.2)
44.0	71.0 (2.1)
53.0	142.3 (5.8)

^aMeasurements by derivative cyclic voltammetry at voltage sweep rates ranging from 1 to 100 Vs^{-1} .

Table 3. Rate constants for the unimolecular decomposition of 9,10-dibromoanthracene anion radical in *N,N*-dimethylformamide.

$T/^{\circ}C$	$((10^{-3})k/s^{-1})^a$
-24.0	8.7(0.4)
-29.5	7.8(0.5)
-35.0	6.3(0.4)
-40.5	4.7(0.3)
-44.0	4.6(0.3)

^aMeasurements by derivative cyclic voltammetry at voltage sweep rates ranging from 200 to 700 Vs^{-1} .

are reported in Tables 2 and 3. A less extensive data set was obtained for *1-c* anion radical. In the latter case, due to the very rapid reaction, low temperatures were required and the data are less reliable than for the other anion radicals.

Kinetic parameters for the anion radical cleavage reactions. Linear regression analyses of the rate constant data were carried out for the reactions in DMF containing Bu_4NBF_4 (0.1 M). The Arrhenius activation energy and the rate constants at 298 K were obtained using eqn. (3). The enthalpy of activation ($\Delta H_{298}^{\ddagger}$) and the entropy of activation ($\Delta S_{298}^{\ddagger}$) were calculated from eqns. (4) and (5), respectively.⁸ The most striking feature of the data (Table 4) is that E_a is nearly independent of

$$\log k = -[E_a/(\ln 10)RT] + \log A \quad (3)$$

$$\Delta H_{298}^{\ddagger} = E_a - RT \quad (4)$$

$$\Delta S_{298}^{\ddagger} = 4.576(\log k - 10.753 - \log T) + E_a/T \quad (5)$$

whether the anion radical is mono- or di-substituted. On the other hand, the rate constants for the mono-substituted anion radicals are about 7.5 times greater than those for the corresponding dihaloanthracene anion radicals. The bromo-substituted anion radicals are about 2000 times as reactive as the corresponding chloro derivatives. Thus, the factor most important in determining the rate of the cleavage reaction is the entropy of activation. The dihaloanion radicals have $\Delta S_{298}^{\ddagger}$ values about 4 cal/(K mol) more negative than those for the mono halo-substituted ions. The 9-chloroanthracene anion radical reaction was accompanied by an entropy change very close to zero while that for the 9-bromoanthracene anion radical was about -22 cal/(K mol).

Table 4. Arrhenius activation parameters for aryl halide anion radical cleavage reactions.^a

Substrate	$E_a/\text{kcal mol}^{-1}$	k_{298}/s^{-1}	$(\Delta H_{298}^\ddagger)^b$	$(\Delta S_{298}^\ddagger)^b$
9-Chloroanthracene	15.2	117.4	14.6	-0.1
9,10-Dichloroanthracene	15.2	15.8	14.6	-4.1
9-Bromoanthracene	4.0 ^c	(2.5×10^5)	(3.4)	(-22)
9,10-Dibromoanthracene	4.0	3.4×10^4	3.4	-26

^a Data from Tables 1-3. ^b Activation parameters calculated according to eqns. (4) and (5) with enthalpy expressed in kcal/mol and entropy in cal/(K mol). ^c Data from 9-bromoanthracene is less reliable than that for the other ions.

The reactions of 9,10-dichloroanthracene anion radical were selected to test for electrolyte and solvent effects. The data are summarized in Table 5. The values of k_{298} , E_a , and $\log A$ are essentially unchanged in going from Bu_4N^+ to Me_4N^+ as the counter ion or from DMF to acetonitrile as the solvent. In addition, the rate constant for the reaction in DMF increased only slightly, 14.0 to 15.8 s^{-1} , in going from Bu_4N^+ concentration of 0.02 to 0.10.

DISCUSSION

The electrochemical cleavage of the carbon-halogen bond has been the topic of considerable debate. Much of the early discussion was centered about the question as to whether or not alkyl halide anion radicals are discrete intermediates in the reactions or if the capture of the electron is accompanied by the concerted cleavage of the carbon halogen bond.⁹ Although a recent *ab initio* calculation led to the conclusion that the solvated methyl chloride anion radical indeed does exist in an energy well with a maximal potential energy barrier of the order of 16 kcal/mol to cleavage,¹⁰ inconsistencies are still apparent.¹¹ The situation is much more clear in the case of aryl halide anion radicals. In many cases, the latter can be observed by cyclic voltammetry¹⁻⁵ and the kinetics of the cleavage reaction have been studied in a number of

cases. The relative stability of anion radicals of haloanthracenes suggested these ions as model substances to obtain detailed kinetic and activation parameter data to serve as a basis for discussion of the energetics of the cleavage reactions.

The difference in enthalpy changes ($\Delta\Delta H_{(6-7)}$) for reactions (6) and (7) can be obtained from the thermodynamic cycle [(8) and (9)] by application



of Benson's additivity rules^{12,13} for reaction (8) and making use of the relative reduction potentials for $\text{Ar}-\text{Cl}$ and $\text{Ar}-\text{Br}$ along with the reduction potentials of X^- which have been estimated (in acetonitrile).¹¹ This leads to eqn. (10) where $\Delta D(\text{Cl}-\text{Br})$ is the difference in dissociation energies

$$\Delta\Delta H_{6-7} = E^\circ(\text{Ar}-\text{Br}) + E^\circ(\text{Cl}^-) - E^\circ(\text{Ar}-\text{Cl}) - E^\circ(\text{Br}^-) + \Delta D(\text{Cl}-\text{Br}) \quad (10)$$

of $\text{Ph}-\text{X}$ bonds. An estimate of $\Delta\Delta H_{6-7}$ can be obtained using (10) assuming that $\Delta D(\text{Cl}-\text{Br})$ does not change in going from $\text{Ph}-\text{X}$ to 9-haloanthracene. This leads to a values of about -4 kcal/mol for the reactions of this study.

If the further assumption is made that the reaction entropies should differ only by the differences in the entropies of solvation of the halide ions (since it is assumed that solvation of the anion radicals does not differ appreciably), $\Delta\Delta S_{6-7}$ can be calculated. The partial molal entropies of LiCl and LiBr have been reported in a number of non-aqueous solvents.¹⁴ The entropy difference for the

Table 5. Kinetic data for the decomposition of 9,10-dichloroanthracene anion radical.

Solvent	(R_4N^+)	$E_a/\text{kcal mol}^{-1}$	k_{298}	$\log A$
DMF	Bu_4N^+	15.2	15.8	12.3
DMF	Me_4N^+	15.3	16.6	12.4
Acetonitrile	Bu_4N^+	14.8	19.2	12.1

two salts in DMF (LiCl–LiBr) is -6.5 cal/(K mol). If the entropies of activation reflect solvation differences between the reactants and the transition states and bond cleavage is nearly complete in the transition states, $\Delta\Delta S_{6-7}^\ddagger$ is thus predicted to approach -6.5 cal/(K mol).

Obviously, since ΔS_{298}^\ddagger is of the order of 20 cal/(K mol) more negative for the reactions of the bromo derivatives than the chloro-substituted anion radicals, the entropy of solvation of the halide ions alone is not the crucial factor. We cannot avoid the conclusion that either (i) the solvation of the transition states differ appreciably depending upon the halogen, or (ii) the solvation and hence structure of the anion radicals depends very much on the identity of the halogen substituents or (iii) a combination of the first two possibilities contributes to the overall effect.

If it is the solvation of the transition states that differs so as to make ΔS_7^\ddagger more negative than ΔS_6^\ddagger , this implies that bond cleavage has progressed to a much greater extent in the case of the bromo-substituted anion radical reactions. Prediction based on the Hammond-Leffler postulate¹⁵ calls for an earlier transition state for the more exothermic reaction. Although the validity of reactivity–selectivity arguments is somewhat controversial,^{15,16} the study of reaction mechanisms has benefited enormously from them. The more complex a reaction is, the more likely that failure in reactivity–selectivity arguments will occur. Thus, the unimolecular decompositions represented by (6) and (7) would appear to be amenable to the use of the Hammond-Leffler postulate. A related, but more complex, case is the E2 elimination of hydrogen halide from aryethyl halides (11). This system appears to be well-behaved with respect to



the Hammond-Leffler postulate with an apparent earlier transition state when X^- is the better leaving group bromide than when hydrogen chloride is eliminated.¹⁷ In the present case, a later transition state could be involved when bromide is involved, since (7) is predicted to be less exothermic than (6), and the degree of carbon–halogen bond breakage in the transition state could be greater. The standard entropy of Br^- in DMF at 298 K has been estimated to be -43.3 cal/(K mol).¹⁴ Thus, if ΔS_{298}^\ddagger is much less negative for the anion radicals, as recent work

on related systems implies,¹⁸ it is plausible that the large negative entropies for the cleavage of the bromo-substituted anion radicals are a consequence of nearly complete bond cleavage in the corresponding transition states. Earlier transition states must then be involved in the cleavage reactions of the chloro derivatives.

The second explanation, that the structures of the chloro- and bromo-substituted anion radicals differ to the extent that the more electronegative chlorine substituent bears an appreciable portion of the negative charge and hence the solvation shell requires little reorganization in going from the reactant to the transition state, appears plausible but less likely than the first. It has recently been shown that during heterogeneous charge transfer reactions involving alternant aromatic hydrocarbons, the origin of the observed differences in entropy is related to the charge distribution in the corresponding ion radicals.¹⁸ Ion radicals with highly diffuse charge distribution are formed with little loss in entropy while formation of those with localized charge is accompanied by larger entropy changes. This was attributed to the degree of solvent orientation in the more highly solvated ion radicals as compared to the substrates. Thus, there is thermodynamic precedent for the kinetic argument which might account for at least part of the large entropy effect.

The third possibility, that a combination of the other two explanations accounts for the observations, cannot be ruled out. Thus, if a somewhat later transition state is involved when the substituent is bromine, this in combination with a more polarized structure for the chloro-substituted anion radicals could account for the fact that ΔS^\ddagger is more negative for the former. However, the very large value of $\Delta\Delta S_{6-7}$ is very puzzling.

Although none of the explanations of the entropy effect are overwhelmingly convincing, related work supports the idea that the origin of the differences lie in the charge distributions. During the reduction of halo-substituted nitrobenzene anion radicals, it has recently been found that the reaction entropies are independent of both the nature of the substituent and the substitution pattern.¹⁷ In all cases ΔS_{298}^\ddagger was found to be small and positive. The nitrobenzene anion radicals are strongly polarized with the charge predominately on the nitro groups regardless of the halo substituent. Thus, in that case there is little difference in ordering of the solvent in the reactant and the transition state.

In this case it is of interest to note that the disubstituted anion radical cleavage reactions are accompanied by entropy decreases of 4 cal/(K mol) more than in the corresponding mono-halo anion radical reactions. This is surely a reflection of the fact that the two halo groups in the symmetrically substituted anion radicals have equal probability of undergoing bond cleavage.

A very pertinent point that must be considered is the effect of measurement error on the magnitude of the activation parameters. The measurement precision using the derivative cyclic voltammetry method has been demonstrated to be of the order of $\pm 5\%$ under conditions where many different experimental variables were changed.⁷ In the experiments described here, very few changes in variables other than the temperature were made for the determination of the activation parameters. Therefore, it is reasonable to conclude that the error in rate constants is considerably less than $\pm 5\%$. The error in the temperature was no more than ± 0.5 K. Therefore, we can take Schaleger and Long's estimates of error in activation parameters²⁰ as maximum values for the work reported here. It appears safe to conclude that the E_a values are in error by no more than about ± 1 kcal/mol and ΔS_{298}^\ddagger are known to about ± 2 cal/(K mol). The differences observed in both E_a and ΔS_{298}^\ddagger are thus far greater than can be expected to arise from measurement error.

In conclusion, attention can once again be focused on the alkyl halide anion radical question. In view of the activation parameters observed for the much less reactive aryl halide anion radical cleavages, it seems that the activation energy for the cleavage of $(\text{CH}_3\text{Cl})^-$ must be much less than the maximum calculated potential energy barrier, 16 kcal/mol.¹⁰ In fact, it seems more plausible that E_a for that reaction will be less than 4.0 kcal/mol, the observed value for the bromoanthracene anion radical reactions.

EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures as well as solvent and electrolyte purification were the same as recently described.²¹ The haloanthracenes were commercial samples and used without further purification. No impurities could be found during cyclic voltammetry studies.

The temperature was controlled by having the cell immersed in cooling baths controlled either

with a cryostat or by virtue of the high heat capacity of water contained in a well-insulated Dewar flask. In all cases, the variation in temperature during the time of the measurements was ± 0.5 K or less. Temperature measurements were made with a Jenway Model 1002 digital thermometer to a precision of ± 0.1 K.

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