

Ion Radical Cleavage Reactions. IV. The Effect of the Halogen in Determining the Mechanism of Cleavage of Halide Ion During the Reduction of 9-Cyano-10-haloanthracenes

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9-Cyano-10-bromoanthracene anion radical undergoes unimolecular cleavage in the expected manner in a number of aprotic solvents. The rate of cleavage was affected significantly by the nature of the solvent, increasing by nearly a factor of 15 in going from butyronitrile to acetonitrile. The activation enthalpies were not sensitive to the solvent (12.2 ± 0.7 kcal/mol) and the activation entropies in three solvents were equal to -8.0 ± 1.5 cal/K mol. In acetonitrile the activation entropy was close to zero which allowed the cleavage reaction to proceed much more rapidly in that solvent. Under the same conditions, unimolecular cleavage of chloride ion from 9-cyano-10-chloroanthracene anion radical was observed to be a minor reaction pathway. The major product of the reactions of the anion radical was 9,9'-bianthryl-10,10'-dicarbonitrile which forms by a higher order reaction. The activation parameters in this case cannot be related to the cleavage of carbon-halogen bonds.

In previous papers in this series¹⁻³ the unimolecular cleavage reactions of some haloaromatic anion radicals have been studied and the activation parameters and rate constants were reported. The activation energies for the cleavage of bromoanthracene¹ and bromobenzophenone³ anion radicals were observed to be significantly lower than those for the corresponding chloro-substituted anion radicals and the rate constants, at 298 K, were of the order of 10^3 larger for the bromo-substituted anion radicals.

We were therefore puzzled by the kinetic data reported by Heinze and Schwart⁴ for the cleavage reactions of 9-cyano-10-haloanthracene anion radicals. They reported activation enthalpies of 3.4 kcal/mol for the chloro-substituted anion radical and 7.3 kcal/mol for the anion radical of 9-cyano-10-bromoanthracene anion radical. The corresponding activation entropies were observed to be -49 and -28 cal/K mol, respectively. This reversal in reactivity and activation energetics appeared to be completely inconsistent with the patterns that were beginning to emerge from the other related studies. We have re-investigated the cleavage reactions in order to attempt to resolve the inconsistencies. In this paper we report the results of kinetic studies on the reactions of both anion radicals and of a product study on the reduction of 9-cyano-10-chloroanthracene.

RESULTS AND DISCUSSION

The cleavage of bromide ion from 9-cyano-10-bromoanthracene anion radical. The cyclic voltammogram of 9-cyano-10-bromoanthracene in propionitrile recorded at 100 mV/s is shown in Fig. 1a. A reversible redox couple (R_2/O_2) was observed following the main reduction peak (R_1). The relative peak height, $I(R_1)/I(R_2)$ was observed to be equal to 1.44. The voltammogram for an equimolar solution of 9-cyano-10-bro-

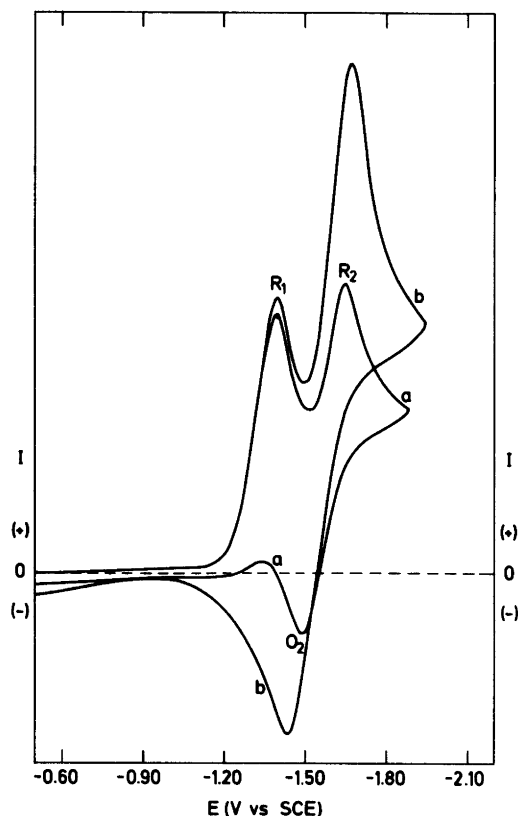
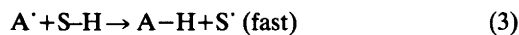
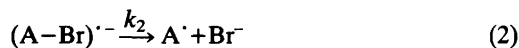
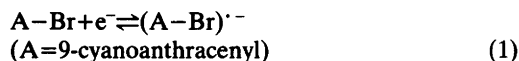


Fig. 1. Cyclic voltammograms of 9-cyano-10-bromoanthracene (2 mM) in propionitrile containing Bu_4NPF_6 (0.05 M). a, Before and b, after the addition of 9-cyanoanthracene (2 mM). Sweep-rate: 100 mV s^{-1} , $t=22^\circ\text{C}$.

moanthracene (2 mM) and 9-cyanoanthracene (2 mM) is shown in Fig. 1b. In this case the reversible couple (R_2/O_2) is enhanced relative to R_1 with $I(\text{R}_1)/I(\text{R}_2)$ equal to 0.71. These voltammograms can be accounted for by reactions (1)–(4) with (1)–(3) taking place at R_1 and (4) at R_2/O_2 .



An alternative to reaction (3) is that A^{\cdot} is first reduced to A^- and then A-H is produced by proton transfer. We do not rule this possibility out nor do we specify the nature of S-H since no information is available regarding these steps. What the data do indicate is that under the time scale of the experiment, reaction (2) is complete and that the yield of 9-cyanoanthracene (A-H) appears to be quantitative under the reaction conditions. These observations justify relating observed rate constants for the decomposition of $(\text{A-Br})^{\cdot-}$ to k_2 . The uncertainty as to whether A-H forms in hydrogen atom transfer reaction (3) or by the alternative pathway involving A^- affects only the magnitude of k_2 evaluated.

The kinetics of the decomposition were studied by derivative cyclic voltammetry.⁵ Rate constants were evaluated assuming mechanism (1)–(3) using theoretical data reported previously.⁶ Kinetic and activation parameters are summarized in Table 1 for reactions carried out in a number of solvents. The data are further illustrated by the Arrhenius plot (Fig. 2) for the experiments carried out in butyronitrile. In this case, rate constant measurements were made at 5 temperatures ranging from 0 – 40.5°C . The linear regression correlation coefficient was 0.999.

An unexpected feature of the data in Table 1 is that the rate of the cleavage reaction was observed to depend on the solvent. The value of k_2 (at 298 K) was about 15 times greater in acetonitrile than in butyronitrile as solvent and about 5.5 times greater in acetonitrile than in DMF. These results should be compared to those reported for the cleavage of 9,10-dichloroanthracene anion radical.¹ In that case very little difference could be detected in either rate con-

Table 1. Kinetic and activation parameters for the cleavage of bromide ion from 9-cyano-10-bromoanthracene anion radical.

Solvent	k_{298}/s^{-1}	$\Delta H_{298}^\ddagger/\text{kcal mol}^{-1}$	$\Delta S_{298}^\ddagger/\text{cal K}^{-1} \text{mol}^{-1}$
DMF ^a	327	12.0	−6.8
DMF ^b	306	11.0	−10.2
AN ^a	1725	13.0	−0.1
Propionitrile ^a	210	12.5	−7.8
Butyronitrile ^b	128	12.4	−7.3

^a Substrate concentration equal to 1.0 mM. ^b Substrate concentration equal to 2.0 mM.

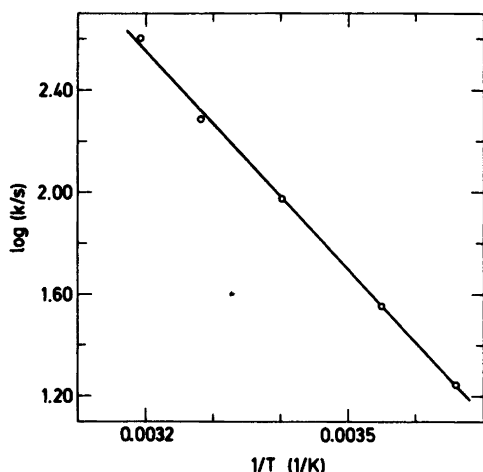


Fig. 2. Arrhenius plot for the cleavage of bromide ion from 9-cyano-10-bromoanthracene anion radical in butyronitrile.

stants or activation parameters in acetonitrile and DMF. A feature of further interest is that the enthalpies of activation, equal to 12.2 ± 0.7 kcal/mol, appear to be independent of the solvent within experimental error. The errors in ΔH^\ddagger and ΔS^\ddagger in related cases¹ have been estimated to be of the order of 1 kcal/mol and 2 cal/K mol taking into account a $\pm 5\%$ error in the rate constants. Thus, the variation in ΔH^\ddagger_{298} observed (Table 1) is within experimental error. The values of ΔS^\ddagger_{298} also appear to be the same, -8.0 ± 1.5 cal/K mol, if the value obtained for the data in acetonitrile are not included. On the other hand, ΔS^\ddagger_{298} was observed to be near zero, -0.1 cal/K mol, in acetonitrile. This value is clearly not within experimental error of the others. Therefore, the only unusual feature of the data in Table 1 is that ΔS^\ddagger_{298} is considerably less negative in acetonitrile than expected based on the other data.

The entropy of activation for the cleavage reactions has previously been discussed¹⁻³ in terms of the differences in solvation of the anion radicals and the transition states leading to the cleavage of the carbon-halogen bond. The standard entropies of the halo-aromatic anion radicals are expected to be, in analogy to the entropies for the formation of hydrocarbon anion radicals,⁷ significantly less negative than those for the formation of halide ions in aprotic solvents.⁸ Assuming the latter to be the case, a ΔS^\ddagger near

zero can be taken to indicate little solvation change in going from the anion radical to the transition state. This implies an early transition state in which little bond cleavage has taken place. If we apply these arguments to the data in Table 1 we arrive at the conclusion that the transition state for the cleavage of bromide ion from 9-cyano-10-bromoanthracene anion radical involves less bond breaking than those for the same reaction in the other solvents. There do not appear to be any trends in the physical properties of the solvents that would predict such solvation differences. On the contrary, DMF and acetonitrile are very similar in such properties as dielectric constant and ion solvating power. Furthermore, no such differences in activation entropies were observed in the related cleavages.^{1,3} Thus, an explanation of the near zero ΔS^\ddagger when acetonitrile is solvent is not apparent.

It is interesting to compare the kinetic and activation parameters observed for the decomposition of 9-cyano-10-bromoanthracene anion radical with those for 9-bromo and 9,10-dibromoanthracene anion radicals. Data are now available for all three processes in DMF. For the cleavage of Br^- from structure 1 where X is either H, Br or CN, the rate constant at 298 K was observed to be 2.4×10^5 , 3.5×10^4 and 3.2×10^2 s^{-1} , respectively. Correlation of $\log k_2$ vs. Hammett σ_p results in ρ equal to -4.4 with a correlation coefficient of 0.998 based on this limited set of data. The activation energies for the cleavage of 1 (X=H and Br) were observed to be the same (3.4 kcal/mol) while the value observed in this study for X=CN was much greater (11.5 kcal/mol). The general trend appears to be that electron withdrawing groups stabilize the anion radicals. This trend is also found in substituted phenyl halides. The anion radicals of bromobenzene and chlorobenzene are very short lived⁹ while those of 4-halobenzophenones^{3,10} react at moderate rates and those derived from 4-halonitrobenzenes^{2,11} react slowly. The very low reactivity of the latter can be rationalized in terms of the localization of charge on the nitro groups of the anion radicals which retards the rate of halide loss.² This same type of stabilization, *albeit* to a lesser extent, can be attributed to other electron withdrawing substituents.

The kinetics of the reactions of 9-cyano-10-

chloroanthracene anion radical. The most unusual feature of the kinetic data presented by Heinze and Schwart⁴ is that relating to a smaller apparent activation energy for the cleavage of chloride ion than for the cleavage of bromide ion even though the chloro-substituted anion radical is much less reactive. This proposal is particularly perplexing when comparisons are made with the parameters for the cleavage of halide ions from 9-haloanthracene anion radicals. In that case the rate constants in DMF were observed to be $2.5 \times 10^5 \text{ s}^{-1}$ for the bromo-substituted anion radical and 117 s^{-1} for the loss of chloride from 9-chloroanthracene anion radical. The corresponding activation enthalpies were observed to be equal to 3.4 and 14.6 kcal/mol. The rate and activation parameters that we observed for the cleavage of bromide from *1* ($X=\text{Br}$) deviate from those reported but the deviations are not too serious in terms of the activation enthalpy, *i.e.* 11.5 kcal/mol in this study as compared to 7.3 kcal/mol reported previously.⁴ On the basis of the relative activation enthalpies observed in the 9-haloanthracene anion radical series, a prediction of greater than 14.6 kcal/mol for ΔH^\ddagger for the cleavage of 9-cyano-10-chloroanthracene anion radical is required in order to be consistent. Thus, the observed value⁴ of 3.4 kcal/mol is clearly inconsistent with the simple cleavage of chloride ion from the anion radical.

Activation energies were determined for the decomposition of 9-cyano-10-chloroanthracene anion radical in both acetonitrile and propionitrile (Table 2). The activation energies were determined by derivative cyclic voltammetry using relationship (5)¹² where $\nu_{0.85}$ refers to the voltage sweep rate necessary for the derivative peak ratio to equal 0.85. The high value of the

$$\ln \nu_{0.85}/T = E_a/RT + c \quad (5)$$

Table 2. Activation energies for the reactions of 9-cyano-10-chloroanthracene anion radical.^a

Solvent	$(\nu_{0.85})_{298}^b/V \text{ s}^{-1}$	$E_a/\text{kcal mol}^{-1}$
AN	1.55	5.4
Propionitrile	0.434	6.7

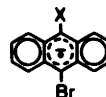
^a In solvent containing Bu_4NBF_4 (0.1 M). ^b The voltage sweep rate necessary for the derivative peak ratio to equal 0.850. Obtained from the correlation line for measurements ranging from 17 to 60 °C.

Table 3. Reaction order analysis of the reaction of 9-cyano-10-chloroanthracene anion radical in acetonitrile.^a

C_A^b/mM	$\nu_{0.85}/V \text{ s}^{-1}$	$\nu_{0.85}/C_A$	$\nu_{0.85}/C_A^{1.25}$
1.00	0.83	0.83	0.83
0.50	0.36	0.72	0.86
0.25	0.15	0.60	0.85

^a In solvent containing Bu_4NBF_4 (0.1 M) at 22.1 °C.

derivative ratio was necessary because of the very low rate of decomposition of the anion radical. The E_a values in Table 2, 5.4 and 6.7 kcal/mol, are higher than those reported earlier⁴ but confirm that the parameter is much lower for the reactions of the chloro-substituted anion radical than for *1* ($X=\text{Br}$).



A reason for the inconsistencies noted above is evident from the data in Table 3. According to the "reaction order approach",¹³ the value of $\nu_{0.85}$ is predicted to be independent of the substrate concentration (C_A) for a first order cleavage of halide ion from the anion radical. The data indicate that the apparent rate constant, proportional to $\nu_{0.85}$, is strongly dependent upon C_A . The last column in Table 3 indicates that the sum of the reaction orders in substrate (A) and anion radical (B) is equal to 2.25. This means that the overall reaction order is greater than 2 under the conditions of the measurements. This suggests some sort of a dimer-forming mechanism rather than a simple halide cleavage reaction.

The products of the decomposition of 9-cyano-10-chloroanthracene anion radical. The products of the reactions of the anion radical were observed to be 9-cyanoanthracene and the dimer, 9,9'-bianthryl-10,10'-dicarbonitrile by preparative electrolysis in both acetonitrile and propionitrile. The dimer was identified by its voltammetric spectrum which consists of six reversible redox couples with oxidation states ranging from +2 to -4.¹⁴ The voltammogram recorded in acetonitrile is illustrated in Fig. 3. The yields of isolated products were <10 and 65 %, for 9-cyanoanthracene and the dimer, respectively,

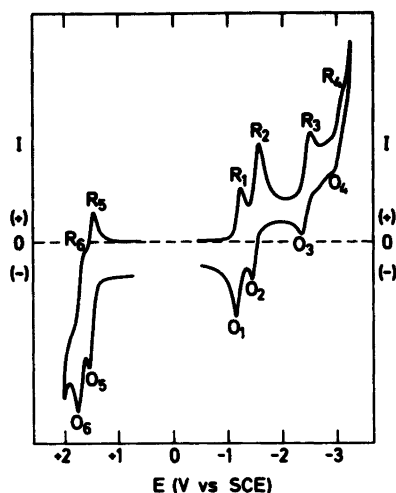


Fig. 3. Cyclic voltammogram of 9,9'-bianthryl-10,10'-dicarbonitrile in acetonitrile containing Bu_4NBF_4 (0.1 M). Sweep-rate: 400 mV s^{-1} , $t=22^\circ\text{C}$.

for the reaction carried out in acetonitrile.

Conclusions. In a number of aprotic solvents, the anion radical generated during reduction of 9-cyano-10-bromoanthracene undergoes unimolecular decomposition with the expulsion of bromide ion. With the exception of a smaller than expected entropy of activation in acetonitrile, the rate and activation parameters for the cleavage reaction are consistent with expectation based on other recent work.¹⁻³ Although some 9-cyanoanthracene is generated during preparative reduction of 9-cyano-10-chloroanthracene, the major product of the decomposition of the anion radical is 9,9'-bianthryl-10,10'-dicarbonitrile. In this case the kinetic studies indicate a higher order mechanism possibly involving a dimerization of the anion radical or the coupling between an anion radical and a neutral molecule. The mechanism of this reaction requires further study. In any event, the activation parameters observed in this case cannot be related to those for the cleavage of chloride ion from the anion radical.

EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures as well as solvent and

electrolyte purification were the same as recently described.¹⁵ 9-Cyano-10-bromoanthracene¹⁶ and 9-cyano-10-chloroanthracene¹⁷ were prepared by standard procedures.

Preparative electrolysis of 9-cyano-10-chloroanthracene. 9-Cyano-10-chloroanthracene (1 mmol, 0.238 g) suspended in acetonitrile (50 ml) containing Bu_4NBF_4 (0.1 M) as supporting electrolyte was subjected to constant current reduction at 12.5 mA for 155 min (1.2 F/mol). The electrodes were platinum gauzes and the cell was divided by a horizontal sintered glass disk (G 3) and a 3 mm layer of neutral alumina at the anolyte side. During the electrolysis all the starting material went into solution and a new yellowish material precipitated out. The product was isolated by filtration followed by several washings with cold acetonitrile and drying. The isolated yield was 131 mg (65 %). The identity of the product was established through its voltammetric behavior as already described. GLC analysis (OV 17, 3 % 280°C) of the filtrate demonstrated that only negligible amounts of starting material were left in solution. The amount of 9-cyanoanthracene formed during the electrolysis was estimated to be less than 10 %.

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