Investigation of the Competition between Electron Transfer and S$_N$2 in the Reaction between Anthracene Radical Anion and the Methyl Halides
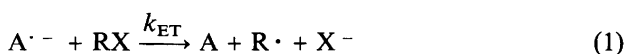
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The mechanism of the reaction between electrogenerated anthracene radical anion and the four substrates trimethylsulfonium iodide, methyl iodide, methyl bromide and methyl chloride in N,N-dimethylformamide has been investigated. By comparing the product distribution for the different methyl systems it is shown that a competition between an electron transfer and an S$_N$2 mechanism exists. Normally aromatic radical anions are considered to be very strong electron donors, but in the cases presented the S$_N$2 mechanism actually constitutes 0, 25, 77 and 97%, respectively, of the two reaction paths. The configuration mixing model is used to give a qualitative interpretation of the experimental results.

The aim of this paper is to present the results of the investigation of the mechanism of the reaction between electrogenerated anthracene radical anion and methyl halides CH$_3$X in N,N-dimethylformamide (DMF). The reaction between aromatic radical anions A·⁻ and alkyl halides RX has attained considerable interest in recent years from both an experimental[1–7] and a theoretical point of view.[7–9] The mechanism generally accepted is described in eqns. (1)–(3). The initial rate-determining step (1) consists of an electron transfer (ET) concerted

$$A^{\cdot -} + RX \xrightarrow{k_{ET}} A + R\cdot + X^-$$ (1)

$$A^{\cdot -} + R\cdot \xrightarrow{k_2} RA^-$$ (2)

$$A^{\cdot -} + R\cdot \xrightarrow{k_3} A + R^-$$ (3)

with the bond-breakage of the carbon–halogen bond followed either by a coupling reaction [eqn. (2)] or a reduction [eqn. (3)] of the thus formed alkyl radical R·. The lifetime of R· is so long that stereochemical equilibration normally occurs. The products RA⁻ and R⁻ will either be protonated or react with RX in a nucleophilic substitution reaction.

In many situations reaction (1) has been used as a model reaction for an ET process[10–12] since the aromatic radical anions have been considered as very strong electron donors. A major concern in this connection is whether step (1) can truly be considered to be an ET or

if it in some cases might be accompanied by an S$_N$2 component as depicted in eqns. (4) and (5). In the rate-determining substitution step (4) bonding between the radi-

$$A^{\cdot -} + RX \xrightarrow{k_{S_N2}} RA\cdot + X^-$$ (4)

$$A^{\cdot -} + RA\cdot \xrightarrow{k_5} A + RA^-$$ (5)
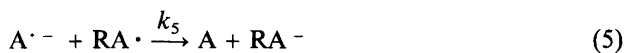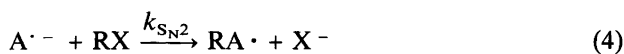
cal anion and the central carbon atom in the alkyl halide occurs, which will lead to inversion at the central carbon atom. The role of the second radical anion is to reduce the coupled radical RA· to the product RA⁻ [eqn. (5)]. Disregarding the stereochemical aspects, the S$_N$2 reaction thus results in the same products as the reaction sequence (1) and (2).

Previously, stereochemical investigations have shown that the process between anthracene radical anion and sterically hindered alkyl halides like bornyl and norbornyl bromide indeed proceeds without any S$_N$2 character.[3] However, when the steric hindrance is diminished in the alkyl system as is the case for optically active 2-octyl halides, the reaction gives detectable amounts of substitution products with inversion. With the iodide, bromide and chloride as leaving groups, the percentage of inversion is 5, 8 and 11, respectively.[4] In this context it is of interest to note that a similar process between quinoxaline radical anion and optically active 2-butyl bromide actually results in racemization.[3] Also the reaction between chemically generated naphthalene radical anion

and the 5-hexenyl halides has been suggested to proceed by a pure ET mechanism.[1]

If an S_N2 component really does exist in some cases, it would be expected to be most pronounced for the methyl halides. Unfortunately an investigation with optically active compounds is not easy achievable in this situation, but still it might be possible to obtain information about the mechanism by comparing the outcome of the reactions between anthracene radical anion and methyl iodide, methyl bromide or methyl chloride. A competition between reaction (1) and (4) should be dependent upon the nature of the halide since the transition state of ET and S_N2 will be influenced to different degrees with a change of leaving group. The more dominant the S_N2 mechanism becomes, the higher the amount of the coupling product CH_3A^- expected as long as the reduction process (3) in the competing ET mechanism is in play. On the other hand, if a pure ET process is occurring for all three CH_3X the product distribution is independent of X.

It should be emphasized that this method only gives a proper estimation of an eventual S_N2 component if a comparison with a standard ET process involving the methyl radical is possible. We propose that the reaction between anthracene radical anion and trimethylsulfonium iodide can be used as such a model process. The existence of any S_N2 component herein does not seem plausible, since the related reaction between anthracene radical anion and tert-butyldimethylsulfonium iodide gives only tert-butylation and no methylation. The latter result can be explained satisfactorily by an ET mechanism as shown in eqn. (1), which will produce the more stable tert-butyl radical instead of the methyl radical.[13]

In this report the ratio $q = [CH_3^-]/([CH_3^-] + [CH_3A^-])$, which can assume values from 0 to 1, is determined in two different ways for the reaction between anthracene radical anion and CH_3X. The first approach is the application of an electrochemical method which has been developed recently.[14] By taking advantage of the steady-state properties of the rotating disk electrode (RDE) an estimation of q (called q_{RDE}) is attainable if it is assumed that the reaction scheme (1)–(5) with the subsequent protonation or nucleophilic reactions constitutes an adequate description. The second approach for determining q (called q_{prod}) consists simply of an analysis by GC of the yield of the coupling product CH_3A^- [isolated either as CH_3AH or $(CH_3)_2A$] produced in reactions (2) and (5) and the amount of A regained in (1), (3) and (5). Both methods are described in detail in the Experimental part.

In Table 1 the average values of q_{RDE} and q_{prod} with their standard deviations are given for each methyl halide and trimethylsulfonium iodide. The agreement between the two sets of values is within the uncertainty range for all four cases. No variation in q_{RDE} and q_{prod} is found as a function of the concentration of A^{-}. The danger of introducing side reactions involving the methyl radical, such as dimerisation or hydrogen atom abstraction due to

Table 1. Values of q_{RDE} and q_{prod} for the reaction between anthracene radical anion and CH_3X at 20 °C in DMF/0.1 M tetrabutylammonium fluoroborate.

Substrate	q_{RDE}	q_{prod}
$(CH_3)_3S^+I^-$	0.62(4)	0.60(5)
CH_3I	0.50(3)	0.46(4)
CH_3Br	0.17(3)	0.15(3)
CH_3Cl	0.00(4)	0.04(4)

inhomogeneity of the reaction solution in the very fast reactions with methyl iodide, thus seems insignificant. Furthermore measurements of q by linear sweep voltammetry give a similar value for MeI.[15]

The most interesting trend in the results is that q is dependent upon the leaving group and decreases with a change from dimethyl sulfide, iodide, bromide and chloride. This indicates a change in the reaction mechanism towards the S_N2 reaction in the leaving group order given. Assuming that the reaction between A^{-} and trimethylsulfonium iodide is a pure ET then the magnitude of the q values shows that the S_N2 mechanism constitutes 21%, 74% and 97%, respectively, of the two reaction paths for the three methyl halides. For methyl chloride the S_N2 mechanism is totally dominant. To our knowledge this is one of the first examples of a reaction between an aromatic radical anion and an alkyl halide proceeding almost exclusively by the S_N2 mechanism. Recently Huang et al.[16] have presented kinetic evidence for a similar mechanism change from ET to S_N2 in the reaction between 1,4-dicyanonaphthalene radical anion and substituted benzyl bromides. A competition between intramolecular ET and S_N2 in radical anions of substituted 1-benzoyl-ω-haloalkanes has also been made plausible by Kimura et al.[17] Preliminary determinations of q_{RDE} for other alkyl halides such as ethyl and butyl halides have shown only a small dependence of q_{RDE} on the nature of the leaving group indicating a clear dominance of the ET mechanism with such substrates.[18]

The change in mechanism with leaving group of the three methyl halides is supported by a concomitant change in the distribution of the coupling products. The coupling products consist of a mixture of 9-methyl- and 9,10-dimethyl-9,10-dihydroanthracene, the ratio of which decreases with an increase in the concentration of the methyl halide and a change of X in the series $(Me)_2S$, Cl, Br and I, and 2-methyl-1,2-dihydroanthracene as proved by authentic samples of these compounds. With trimethylsulfonium iodide, methyl iodide, methyl bromide and methyl chloride the ratio of substitution products in the 9- and 2-position of anthracene is 1:1.4, 1.4:1, 7.0:1 and 50:1, respectively.

The steric conditions at the different positions in the anthracene radical anion will probably play only a minor role in the product distribution owing to the small size of the methyl halides and the methyl radical. From a qualitative point of view, the radical coupling [eqn. (2)] in the ET mechanism would therefore be expected to take place

mainly at the 9-position which has the highest spin density.[19] However, with trimethylsulfonium iodide as the substrate, the favourable position of attack is in fact at position 2 and it seems likely that the spin density is not always a reliable guide for a prediction of the product distribution. Such a phenomenon has been observed previously. For instance, with isoquinoline radical anions, attack at position 1 or 8 would be expected from the EPR spectrum but the actual attack from the tert-butyl radical occurs at position 6.[20] It may be that the tert-butyl radical is too sterically hindered for a correct assessment in this case but on the other hand, the reductive tert-butylation of pyrene does follow the spin densities.[20a]

The experimental results also indicate that the more dominant S_N2 mechanism becomes, the higher the amount of substitution in the 9-position of anthracene. If the S_N2 mechanism is assumed to proceed exclusively by 9-substitution and if the ratio of 9- and 2-substitution found for trimethylsulfonium iodide is the one to be expected for an ET mechanism, then the product distributions may with some caution be used to describe the importance of S_N2 in the three reactions in question. The percentage of S_N2 hereby obtained is 29, 79 and 97 in the sequence X = I, Br and Cl, which is in accordance with the numbers calculated from the q values. The two sets of results derived from q and the distribution of coupling products are summarised in Table 2.

The reactions studied here are kinetically controlled and the product distribution reflects the energy of the transition state. The relevant parameters are therefore the activation barriers, which may be described by use of the configuration mixing (CM) model.[21] According to this model the activation barrier of a reaction arises as the result of an avoided crossing of potential energy curves that link the reactants in their ground state with an excited state of the product configuration and an excited state of the reactants with the products in their ground state. In the following discussion we intend to use the CM model in a qualitative interpretation of the experimental results presented in this report.

The barriers $\Delta E_{ET}^{\ddagger}$ and $\Delta E_{S_N2}^{\ddagger}$ for the ET and S_N2 process can be estimated as given in eqns. (6) and (7), where $\Delta E_{ST}(\pi\pi^*)$ is the singlet–triplet excitation energy

$$\Delta E_{ET}^{\ddagger} = f_{ET}(I_{A^{\cdot -}} - EA_{CH_3X}) - B_{ET} = f_{ET}\Gamma_{ET} - B_{ET} \quad (6)$$

$$\Delta E_{S_N2}^{\ddagger} = f_{S_N2}[I_{A^{\cdot -}} - EA_{CH_3X} + \Delta E_{ST}(\pi\pi^*)] - B_{S_N2}$$
$$= f_{S_N2}\Gamma_{S_N2} - B_{S_N2} \quad (7)$$

of anthracene (176 kJ mol^{-1}),[22] f is a curvature factor (≈ 0.20–0.25), B is the avoided crossing parameter, $I_A^{\cdot -}$ is the vertical ionization potential of $A^{\cdot -}$ and EA_{CH_3X} is the vertical electron affinity of CH_3X in solution. Association constants have been omitted since the influence of such terms is expected to be small.[23] The expressions given in parentheses in eqns. (6) and (7) describe the energy gaps Γ between the ground state and the singly and doubly excited states of the reactants, respectively. The singlet–triplet excitation energy $\Delta E_{ST}(\pi\pi^*)$, which is included in the barrier for the S_N2 mechanism in order to account for the bonding nature of this process, will clearly favour the ET mechanism. Unfortunately the magnitudes of the curvature factors f_{ET} and f_{S_N2} cannot easily be predicted. The latter factor is expected to be a bit lower than the former owing to the more exergonic nature of the S_N2 mechanism, although electron delocalization of the odd electrons in ^3A will have some opposing effect. Solvation effects may also influence f_{ET} and f_{S_N2} but if f_{ET} in a simple approximation is assumed to be equal to f_{S_N2}, then it follows that the S_N2 mechanism can offer the ET mechanism competition, as is the case for the methyl halides, only if B_{S_N2} is about 40 kJ mol^{-1} higher than B_{ET}. In the transition states of the S_N2 and the ET reactions the reactants will be oriented in a manner which optimizes the B values, i.e., the interaction between the π-HOMO orbital of anthracene radical anion and the σ^*-LUMO orbital of CH_3X, and the π^*-SOMO orbital of anthracene radical anion and the σ^*-LUMO orbital of CH_3X, respectively. For the ET mechanism the resonance stabilization energy is expected to be small due to the non-bonding character of this mechanism, even though it should be pointed out that recent experiments[5,6] have indicated B_{ET} values in the order of 10 kJ mol^{-1}. A cautious estimation of an average value of B_{S_N2} for the methyl halides is therefore as much as 50 kJ mol^{-1}, a value which reflects the substantial bond coupling in the transition state and shows that aromatic radical anions may act as strong nucleophiles under suitable conditions. When the central carbon atom in the alkyl halide becomes a little more sterically hindered than in the case of the methyl halides, the distance between the reactants in the transition state will increase. The result is a lowering of the value of B_{S_N2} compared with B_{ET} and the balance is tipped in favour of the ET mechanism.

The present investigation also showed that the S_N2 mechanism progressively replaces the ET mechanism for CH_3X in the sequence X = $(CH_3)_2S$, I, Br and Cl. From a thermodynamic point of view the competition between the S_N2 and ET mechanism should be independent of the leaving group since the difference in driving force between the two reaction paths, $\Delta\Delta G_{S_N2-ET}^{\circ}$, is simply given by

Table 2. The percentage of S_N2 mechanism in the reaction between anthracene radical anion and CH_3X at 20 °C in DMF/0.1 M tetrabutylammonium fluoroborate as determined by measurements of q and the distribution of coupling products. The uncertainty is ±5%.

Substrate	q measurements	Coupling product distribution
$(CH_3)_3S^+I^-$	0	0
CH_3I	21	29
CH_3Br	74	79
CH_3Cl	97	97

eqn. (8), where ΔG_f° is the Gibbs energy of formation.

$$\Delta\Delta G_{S_N2\text{-}ET}^\circ = \Delta G_f^\circ(CH_3A\cdot) - \Delta G_f^\circ(A) - \Delta G_f^\circ(CH_3\cdot) \quad (8)$$

From a kinetic point of view the relevant term to regard is $\Delta E_{S_N2}^\ddagger/\Delta E_{ET}^\ddagger$ and according to the CM model the development in this ratio as a function of X depends on the changes in f, Γ and B. Unfortunately, the small overall effect of these three parameters on $\Delta E_{S_N2}^\ddagger/\Delta E_{ET}^\ddagger$ is not predictable even on a qualitative basis and the trend in the experimental results can therefore not be confirmed. However, in this context it suffices to conclude that the CM model substantiates the experimental findings of a connection between the nature of the leaving group and the competition between S_N2 and ET.

Experimental

Materials. Anthracene, trimethylsulfonium iodide, methyl iodide, methyl bromide and methyl chloride were obtained commercially and used as received. N,N-Dimethylformamide and tetrabutylammonium tetrafluoroborate (TBABF$_4$) were purified by standard procedures. 9-Methyl-9,10-dihydroanthracene,[24] 9,10-dimethyl-9,10-dihydroanthracene[24] and tert-butyldimethylsulfonium iodide[25] were prepared according to the references given. These compounds were all recrystallized from ethanol before use. 2-Methyl-1,2-dihydroanthracene was prepared from an electrochemical reduction ($E = -1.9$ V vs. SCE) of 200 mg anthracene in the presence of 1 g trimethylsulfonium iodide in DMF/0.1 M TBABF$_4$. When the reduction was finished, water was added and the coupling products were extracted with diethyl ether, which was washed free of DMF with water. After drying, the solvent was removed *in vacuo* and 2-methyl-1,2-dihydroanthracene was separated as the first product from the crude sample by chromatography through a silica gel column with petroleum ether as the eluent.

Apparatus. The ^{1}H NMR spectra were recorded with a Varian Gemini 200 MHz spectrometer. GC was performed with a Hewlett-Packard 5890 gas chromatograph with an HP-1 column: injector temperature 250 °C; 60 °C for 15 min to 250 °C at 5 °C min^{-1}. For the GC–MS analyses a Hewlett-Packard 5890 gas chromatograph with an HP-1 column combined with a VG Masslab mass spectrometer was used. The electrochemical cell used was an H-cell and the electrodes a rotating disk electrode, a platinum net, a carbon electrode and a silver wire in DMF/0.1 M TBABF$_4$ reference electrode. The rotating disk electrode system (Metrohm 628-10, glassy carbon electrode with $\phi = 3$ mm) was obtained commercially. The signals from a home-built potentiostat used for the potentiostatic measurements were recorded using a Nicolet 4094c/4570 digital oscilloscope. The equipment was controlled by means of a PC. The preparative reductions

were carried out with a 200 W home-built three-electrode potentiostat.

Procedure. The method for determining q_{RDE} has been described in detail elsewhere[14] and therefore only a short description will be given here. The measurements were performed by reducing a given amount of anthracene electrochemically at the platinum net ($E = -1.9$ V vs. SCE) to its relatively stable radical anion followed by addition of the methyl halide. By comparing the current changes in the steady-state voltammograms at a rotating disk electrode for the A/A$\cdot$ $^-$ couple recorded before and after the addition of the methyl halide it is possible to calculate q_{RDE} from eqn. (9), where D_A and $D_{A\cdot^-}$

$$q_{RDE} = 2\left(\frac{D_A}{D_{A\cdot^-}}\right)^{-2/3}\left(\frac{\Delta i_A}{\Delta i_{A\cdot^-}}\right) - 1 \quad (9)$$

are the diffusion coefficients of anthracene and its radical anion. The current change Δi_A is the increase in the cathodic current due to the production of anthracene in the reactions (1), (3) and (5), while $\Delta i_{A\cdot^-}$ is the decrease in the anodic current due to depletion of A$\cdot$ $^-$ in the reactions [(1)–(5)]. The concentration of the methyl halide added to the solution was always kept below half the concentration of A$\cdot$ $^-$ in order to prevent any contribution to the current change Δi_A from a direct reduction of CH$_3$X. While trimethylsulfonium iodide, methyl iodide and methyl bromide could be added directly to the solution, a saturated DMF solution was used in the case of the gaseous methyl chloride. For each methyl halide the measurement of q_{RDE} was performed for at least four different concentrations of A$\cdot$ $^-$ in the range 2–10 mM. As an illustration of the absence of changes in q_{RDE} as the initial concentration of A$\cdot$ $^-$, $C_{A\cdot^-}$, is changed it may be mentioned that the following series of ($C_{A\cdot^-}$, q_{RDE}) values was obtained for methyl iodide: (9.9 mM, 0.49), (8.2 mM, 0.46), (5.9 mM, 0.50), (4.0 mM, 0.54) and (2.4 mM, 0.50).

The experimental procedure for determining q_{prod} was as follows. A given amount of anthracene (8 mM) was partially reduced at the platinum net to its radical anion, the concentration of which could be determined from steady-state curves recorded before and after reduction, taking into account the known values of the diffusion coefficients $D_{A\cdot^-}$ and D_A.[14] For each CH$_3$X three different concentrations of A$\cdot$ $^-$ were used, namely 2, 4 and 6 mM. The methyl halide was then added in excess to ensure that all A$\cdot$ $^-$ reacted. The amount of anthracene and coupling products formed was determined by GC using naphthalene as an internal standard. Methane or ethane produced from the protonation of CH$_3$ $^-$ or the nucleophilic substitution reaction with CH$_3$X were not trapped. When dihydroanthracene was detected in the GC sample the results were discarded in order to avoid any contribution to the formation of substitution products from an S_N2 reaction between dihydroanthracene anion and the methyl halide. The dihydroanthracene an-

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ion is probably produced from a protonation of an-thracene radical anion followed by reduction of the thus formed radical. The formulas for the calculation of q_{prod} from the yields of RA$^-$ and A are given by eqns. (10) and (11), where n_A^* and $n_{A^-}^*$ are the number of moles of A and A$^-$ before addition of the methyl halide as deter-

$$q_{prod} = 1 - \frac{2n_{RA^-}}{n_{A^-}^*} \qquad (10)$$

$$q_{prod} = \frac{2(n_A - n_A^*)}{n_{A^-}^*} - 1 \qquad (11)$$

mined from steady-state voltammograms, while n_A and n_{RA^-} are the number of moles of A and RA$^-$ after the addition of CH_3X as determined by GC. The agreement between the values obtained from eqns. (10) and (11) was good.

Reduction of anthracene and CH_3X. The coupling products found were identified by GC–MS and NMR analysis in comparison with authentic samples.

9-Methyl-9,10-dihydroanthracene, ^1H NMR spectrum ($CDCl_3$): δ 1.58 (d, 3 H, $J = 7.2$ Hz), 4.03 (d, H_{10}, $J = 18.3$ Hz), 4.19 (q, H_9, $J = 7.2$ Hz), 4.27 (d, $H_{10'}$, $J = 18.3$ Hz), 7.30–7.50 (m, 8 H). Mass spectrum [m/z (%)]: 194 (10), 179 (100), 178 (43), 152 (5), 89 (6).

9,10-Dimethyl-9,10-dihydroanthracene, ^1H NMR spectrum ($CDCl_3$): δ 1.59 (d, 6 H, $J = 7.3$ Hz), 4.11 (q, 2 H, $J = 7.3$ Hz), 7.20–7.35 (m, 8 H). Mass spectrum [m/z (%)]: 208 (11), 194 (15), 193 (100), 179 (13), 178 (74), 165 (6), 152 (5), 89 (6).

2-Methyl-1,2-dihydroanthracene, ^1H NMR spectrum ($CDCl_3$): δ 1.15 (d, 3 H, $J = 6.7$ Hz), 2.60–3.15 (m, 3 H), 5.99 (dd, H_3, $J = 9.6$ Hz, 3.2 Hz) 6.60 (dd, H_4, $J = 9.6$ Hz, 1.5 Hz), 7.35–7.80 (m, 6 H). The attribution of these signals to the 2-isomer instead of the 1-isomer was sub-stantiated by a COSY experiment. The COSY spectrum showed a small allylic coupling between H_3 and H_2, the latter having a large coupling constant to the CH_3 group. ^{13}C NMR spectrum ($CDCl_3$): δ 136.9, 134.5, 133.5, 133.4, 132.9, 128.1, 127.6, 127.4, 126.2, 126.0, 125.8, 124.4, 37.1 (CH_2), 29.9 (CH), 20.7 (CH_3). Mass spectrum [m/z (%)]: 194 (55), 179 (100), 178 (64), 165 (25), 152 (8), 89 (6).

Small amounts of, presumably, 1-methyl-1,2-dihy-droanthracene were detected by GC–MS. Mass spec-trum [m/z (%)]: 194 (49), 179 (100), 178 (56), 165 (16), 152 (7), 89 (8).

Reduction of anthracene and tert-*butyldimethylsulfonium io-dide.* The coupling products found were identified as 9-*tert*-butyl-9,10-dihydroanthracene, 2-*tert*-butyl-1,2-dihy-droanthracene and 1-*tert*-butyl-1,2-dihydroanthracene in the isomer ratio 2.7:1.3:1 by comparison with the known result[10] from a reduction of anthracene in the presence of *tert*-butyl bromide (isomer ratio 3.4:1.5:1).

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