Activation parameters for the competing electron transfer and S_N2 pathways of the reaction of anthracene radical anion with cyclopropylmethyl bromide

Henrik Jensen, Heidi Skovbak Sørensen, Steen Uttrup Pedersen and Kim Daasbjerg *

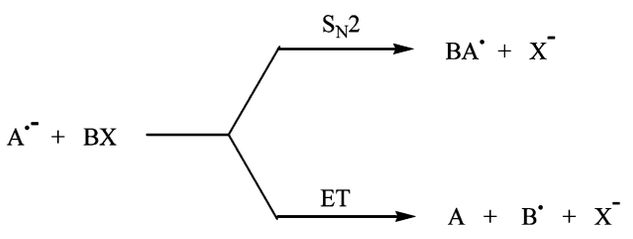
Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark. E-mail: kdaa@chem.au.dk; Fax: +4586196199

Received (in Cambridge, UK) 19th April 2002, Accepted 5th June 2002
First published as an Advance Article on the web 3rd July 2002

The reaction between the electrogenerated radical anion of anthracene and alkyl halides has been studied in the temperature interval of −50 to 40 °C in *N*,*N*-dimethylformamide in order to describe in detail the competition between the electron transfer (ET) and S_N2 pathways. For cyclopropylmethyl bromide the competition can be quantified directly on the basis of an analysis of the distribution of ring-opened *versus* ring-closed products. In general, the ET pathway is found to prevail although the S_N2 pathway becomes of greater importance as the temperature is lowered. When the product analysis is combined with the measurement of the overall rate constant for the reaction the pertinent activation parameters can be extracted for both mechanisms. As expected $\Delta H^{\ddagger}_{S_N2}$ is smaller than $\Delta H^{\ddagger}_{ET}$ (by 7 kJ mol^{-1}) because of the stronger bonding interaction present in the transition state of S_N2. On the other hand, this effect is more than counterbalanced by the fact that ET is entropically favoured because of smaller geometrical restrictions ($\Delta S^{\ddagger}_{ET} - \Delta S^{\ddagger}_{S_N2} = 37$ J mol^{-1} K^{-1}). The S_N2 mechanism leads to substitution in the 9 position of anthracene while for the ET mechanism it takes place in all three positions of 1, 2 and 9. The overall distribution of products in the three positions is largely independent of temperature. This is due to the fact that the increased amount of S_N2 products formed in the 9 position as the temperature is lowered is accompanied by an equally large decrease in the amount of ET products obtained in the very same position. Exactly the same constancy in the product distribution is seen for the reaction of anthracene radical anion with bromoethane, where both mechanisms also exist. For the reaction involving the sterically hindered 1-iodoadamantane, on the other hand, the S_N2 pathway is precluded and in this case there is a profound decrease in the amount of 9-substitution as the temperature is lowered.

Introduction

Electron transfer (ET) reactions constitute essential steps in many important mechanisms.[1,2] This was shown early to be the case for the now well-established $S_{RN}1$ mechanism[3–5] but also for other nucleophilic substitution reactions previously believed to proceed by the S_N2 mechanism the rate-controlling step can be an ET with essentially no stabilisation of the transition state under appropriate conditions.[6] One particularly interesting case in this context is presented by the reaction of aromatic radical anions, $A^{\bullet -}$, with alkyl halides, BX, because of the dichotomy present between the S_N2 and ET pathways as depicted in Scheme 1.



Scheme 1

While the S_N2 pathway results in the formation of a new bond between the A and B parts, *i.e.* $BA^{\bullet}$, the aromatic compound A and the radical $B^{\bullet}$ are generated in the ET pathway.

From a historical point of view the ET process was believed to be completely dominant because of the formation of the stable aromatic compound. It has served numerous applications, *i.e.* in the indirect reduction of different substrates,[7,8] in the redox catalysis approach for measuring rate constants[9–14] and as a model reaction for describing substitution[6] and dissociative ET processes.[15–17] The main advantages of using aromatic radical anions as ET donors are related to their easy generation from the parent aromatic compounds through electrochemical reduction, their well-known standard oxidation potential and self-exchange reorganisation energy as well as the fact that the odd electron is delocalised making it less accessible for bonding interactions with the electrophile. Indeed, it has been shown that the ET pathway prevails for sterically hindered substrates, *i.e. tert*-butyl, neopentyl and adamantyl halides, whereas the situation is more complex for simple substrates, *i.e.* methyl, butyl and 2-butyl halides.[18–20] In the reaction between the radical anion of anthracene and optically active 2-octyl iodide, bromide and chloride it was found that the S_N2 component constituted 5, 8 and 11%, respectively, at room temperature.[18] Recently, it was reported that the S_N2 pathway for the reaction between a number of radical anions and alkyl halides could even be the dominant one as determined from leaving group effects and substitution patterns of the products formed.[19,20] For the reaction between the radical anion of anthracene and chloromethane, the S_N2 component was estimated to constitute as much as 97%. The S_N2 percentage decreased if the electron-donating ability of the radical anion was enhanced by selecting an aromatic compound with a lower (*i.e.* more negative) standard potential or if the electron-accepting ability of the substrate was enhanced by going from X = Cl to I.

An interesting issue pertains to the structure of the transition

DOI: 10.1039/b203858g

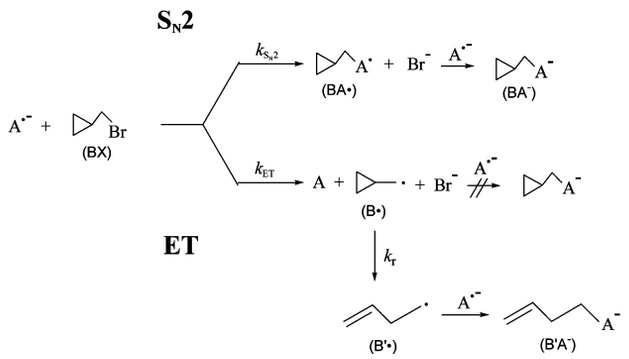
states for the two mechanisms. While the transition state of an S_N2 process is highly ordered there should be essentially no geometrical restrictions on an outer-sphere ET reaction. On the other hand, theoretical considerations have indicated that the transition state of inner-sphere ET reactions involving just a few kcal mol^{-1} of interaction may be quite well-ordered.[21–30] Experimentally, the extraction of activation entropies from Arrhenius plots did reveal that they were larger (*i.e.* less negative) for the reactions of aromatic radical anions with sterically hindered alkyl and benzyl halides than for the reactions with the simple halides, where the S_N2 component was present.[31,32] Since both mechanisms operate at the same time in the latter cases mechanistic changes induced by a lowering of the temperature should in principle be feasible. Unfortunately, the Arrhenius plots obtained were not able to support this interpretation as they were all found to be best represented by a single straight line, independent of the alkyl halide studied. In fact, in the literature only one report has appeared concerning product studies of the reaction between the radical anion of anthracene and optically active 2-octyl halides at two different temperatures, where a lowering of temperature was found to favour the S_N2 mechanism.[18]

In the present paper our aim is to present a systematic study of the temperature dependency of the competition between the two reaction pathways in order to extract the pertinent activation parameters. Since the previous studies showed that the competition exists mainly for methyl halides and primary and secondary alkyl halides we selected cyclopropylmethyl bromide as a model compound. The interesting feature of this particular alkyl halide is that the cyclopropylmethyl radical generated in an ET pathway can undergo ring opening, thereby providing direct access to a quantification of the amount of products formed in the ET and S_N2 pathways at different temperatures. In particular, this would give the opportunity of obtaining for the first time an absolute measure of the entropies of activation for the two competing mechanisms. The substrates bromoethane and 1-iodoadamantane were included in the investigation in order to complete the picture of the different factors affecting the competition. As model compound for the aromatic radical anions we employed the electrochemically generated radical anion of anthracene, the nucleophilic and electron-donating abilities of which are well-known.[18–20] At the same time our previous studies had revealed that the product pattern for this radical anion would be strongly dependent on the mechanism;[19,20] while the S_N2 reaction leads to substitution in the 9 position of anthracene, all three positions, 1, 2 and 9, are accessible for the ET mechanism.

Results and discussion

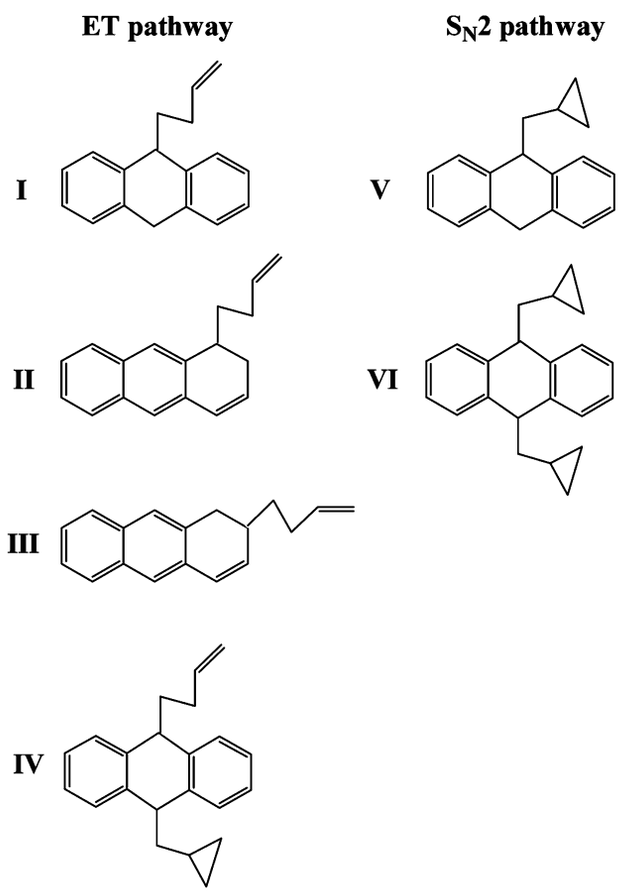
The complete mechanistic scheme for the S_N2 and ET pathways involving $A^{\bullet -}$ and cyclopropylmethyl bromide is depicted in Scheme 2.[18–20,33] †

In the S_N2 mechanism, the substitution product, $BA^{\bullet}$, is formed directly in the first step between $A^{\bullet -}$ and BX with a rate constant k_{S_N2} followed by its further reduction to BA^-. This anion will either be protonated to afford BAH or eventually react with BX in another substitution reaction to give B_2A. Note that these products will always contain the cyclopropyl ring as there is no possibility for a ring opening in the S_N2 mechanism. For the ET mechanism, on the other hand, the situation is quite different. Here the cyclopropylmethyl radical,



Scheme 2

$B^{\bullet}$, formed initially upon the dissociative ET from $A^{\bullet -}$ to cyclopropylmethyl bromide with the rate constant k_{ET} rearranges rapidly to give the corresponding butenyl radical ($k_r = 9.4 \times 10^7$ s^{-1}), $B'^{\bullet}$.[36] As a consequence, the substitution product formed in the follow-up reaction between $B'^{\bullet}$ and $A^{\bullet -}$ (rate constant $\approx 10^9$ M^{-1} s^{-1}) [37] will contain a butenyl group as substituent rather than the cyclopropyl ring. This product, denoted by $B'A^-$, will like BA^- either be protonated to yield B′AH or react with BX in a nucleophilic substitution reaction to give B′BA. In principle, the ET mechanism might lead to the production of the very same products BAH and B_2A as obtained in the S_N2 mechanism, if $B^{\bullet}$ is intercepted by $A^{\bullet -}$ prior to the ring opening process. Experimentally, however, this reaction is easily avoided simply by employing a low concentration of $A^{\bullet -}$ as described in the experimental part. It should also be emphasised that $A^{\bullet -}$ will not be able to reduce either of the two primary alkyl radicals $B^{\bullet}$ or $B'^{\bullet}$ to their corresponding anions.[38,39] From the above discussion it follows that the substitution products formed in the present investigation can be attributed to the S_N2 or ET pathways according to the list given in Scheme 3.



Scheme 3

† The use of cyclopropylmethyl bromide in the quantification of the S_N2 character bears a strong resemblance to the use of radical clocks such as 6-iodohex-1-ene in earlier mechanistic investigations.[34] These results were later criticised since the cyclised radical formed upon ET to 6-iodohex-1-ene is capable of abstracting an iodine from the substrate.[35] Such complications can be ignored for alkyl bromides which are much less prone to be involved in halogen abstraction reactions.

Note that the S_N2 process results in substitution in the 9 position while for the ET process the substitution takes place in all three positions 1, 2 and 9, in accordance with previous assessments.[19,20] The relative amount of double and mono alkylated products varies from experiment to experiment, depending on the relative amount of BX and residual water (protonation source) present in solution. In no experiments did we observe the formation of the double alkylated analogs of **II** and **III** which shows that the protonation of $B'A^-$ in these cases is substantially faster than the further alkylation process.

Activation parameters

The reaction between the electrochemically generated radical anion of anthracene and cyclopropylmethyl bromide was studied at different temperatures T ranging from −50 to 40 °C in *N*,*N*-dimethylformamide (DMF). The products were analysed by means of GC–MS and NMR. In Table 1 we have collected the distribution of the products as a function of temperature along with the S_N2 and ET components calculated according to the formula: $\%S_N2 = ([\mathbf{V}] + [\mathbf{VI}]) \times 100\%/([\mathbf{I}] + [\mathbf{II}] + [\mathbf{III}] + [\mathbf{IV}] + [\mathbf{V}] + [\mathbf{VI}])$ and $\%ET = 100\% - \%S_N2$. The trend in these results is distinct in the sense that the S_N2 component increases as the temperature is lowered although it does not become the major mechanism in the present temperature interval.‡ This is also illustrated by the plot in Fig. 1 of $R\ln(\%S_N2/\%ET)$ against T^{-1}, where R denotes the molar gas constant.

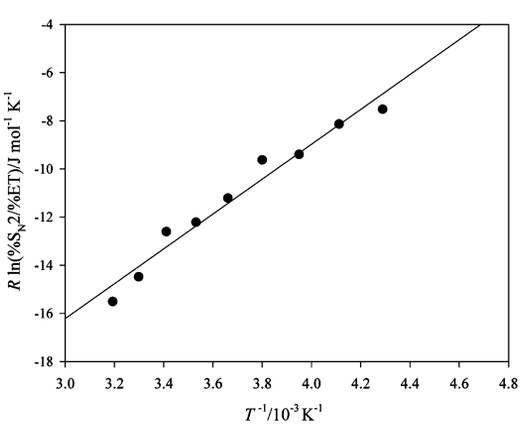


Fig. 1 Plot of $R\ln(\%S_N2/\%ET)$ *vs.* T^{-1} for the reaction between the radical anion of anthracene and cyclopropylmethyl bromide in 0.1 M Bu_4NBF_4–DMF.

The slope and the intercept of the plot hold important information about the activation parameters of the two reactions. On the basis of the Arrhenius equation the rate constants k_{S_N2} and k_{ET} can be expressed as shown in eqns. (1) and (2).[40]

$$k_{S_N2} = A_{S_N2} \exp(-E_a^{S_N2}/RT) \quad (1)$$

$$k_{ET} = A_{ET} \exp(-E_a^{ET}/RT) \quad (2)$$

The parameter A denotes the pre-exponential factor and E_a is the activation energy. According to transition state theory, A and E_a can be expressed through eqns. (3) and (4).

$$A = \frac{ek_BT}{h} \exp(\Delta S^{\ddagger}/R) \quad (3)$$

$$E_a = \Delta H^{\ddagger} + RT \quad (4)$$

‡ A few experiments carried out on the reaction between the radical anion of azobenzene and cyclopropylmethyl bromide showed that the S_N2 component constituted as much as 90% at room temperature. The greater importance of the S_N2 mechanism in this case is related to the fact that the radical anion of azobenzene with a standard potential of −1.279 V *vs.* SCE is a poorer electron donor than the radical anion of anthracene with a standard potential of −1.890 V *vs.* SCE.

Table 1 Molar distribution of products **I–VI** obtained in the reaction between the radical anion of anthracene and cyclopropylmethyl bromide at different temperatures in 0.1 M Bu_4NBF_4–DMF. The amount of **III** is set to 100. The S_N2 and ET constituents are calculated as: $\%S_N2 = ([\mathbf{V}] + [\mathbf{VI}]) \times 100\%/([\mathbf{I}] + [\mathbf{II}] + [\mathbf{III}] + [\mathbf{IV}] + [\mathbf{V}] + [\mathbf{VI}])$ and $\%ET = 100\% - \%S_N2$. The uncertainty is estimated to be ±1.5%

	ET products			S_N2 products		
T/°C	**I** + **IV**	**III**	**II**	**V** + **VI**	$\%S_N2$	%ET
−50	92	100	23	104	32.6	67.4
−40	106	100	29	95	28.8	71.2
−30	103	100	26	86	27.3	72.7
−20	125	100	29	82	24.4	75.6
−10	124	100	28	79	23.9	76.1
0	119	100	31	65	20.6	79.4
10	123	100	34	59	18.7	81.3
20	131	100	34	58	18.0	82.0
30	132	100	36	47	14.9	85.1
40	122	100	43	41	13.4	86.6

Here k_B denotes the Boltzmann constant, h is the Planck constant, $\Delta S^{\ddagger}$ is the entropy of activation and $\Delta H^{\ddagger}$ the enthalpy of activation. Note that the above expression for A pertains to the gas phase with the value of ek_BT/h being equal to 1.7×10^{13} M^{-1} s^{-1} at 298 K. For solution reactions the relevant value is probably about 3×10^{11} M^{-1} s^{-1}.[41] In that instance, previously published entropies of activation[31,32] will be underestimated by approximately 34 J mol^{-1} K^{-1}. However, in the need of a more accurate estimation of the pre-exponential factor we will use the value of ek_BT/h in the case of both A_{S_N2} and A_{ET}, since this will allow us to compare directly the present results with previous measurements.

By combining eqns. (1) and (2) it now becomes possible to derive a theoretical expression for the ratio of the S_N2 and ET components, $\%S_N2/\%ET$, as shown in eqn. (5).

$$\%S_N2/\%ET = k_{S_N2}/k_{ET} = (A_{S_N2}/A_{ET}) \exp[(E_a^{ET} - E_a^{S_N2})/RT] \quad (5)$$

Insertion of eqn. (3) in eqn. (5) leads to eqn. (6).

$$R\ln(\%S_N2/\%ET) = (\Delta S^{\ddagger}_{S_N2} - \Delta S^{\ddagger}_{ET}) + (E_a^{ET} - E_a^{S_N2})/T \quad (6)$$

Hence, the plot of $R\ln(\%S_N2/\%ET)$ against T^{-1} in Fig. 1 is predicted to be linear with a slope equal to the difference in the activation energies (or activation enthalpies) and an intercept equal to the difference in the activation entropies. The following values ensue:

$$E_a^{ET} - E_a^{S_N2} = \Delta H^{\ddagger}_{ET} - \Delta H^{\ddagger}_{S_N2} = 7 \text{ kJ mol}^{-1}$$
$$\Delta S^{\ddagger}_{ET} - \Delta S^{\ddagger}_{S_N2} = 37 \text{ J mol}^{-1} \text{ K}^{-1}$$

In order to obtain the absolute values of the activation parameters a determination of the rate constants k_{S_N2} and k_{ET} is required. Fortunately, the observable rate constant $k_{obs} = k_{S_N2} + k_{ET}$ is easily measured by means of cyclic voltammetry in the very same temperature interval of −50 to 40 °C. On the basis of the values of $\%S_N2$ and %ET listed in Table 1 the specific rate constants can subsequently be extracted. These rate data are collected in Table 2.

In Fig. 2 Arrhenius plots are made for k_{obs}, k_{ET} and k_{S_N2}. In principle, it should be possible to observe a transition in the plot of $\ln k_{obs}$ *vs.* T^{-1}, since two mechanisms are operating simultaneously. However, as is evident from the figure the ET mechanism is dominating and the pertinent activation energies are too close to allow the observation of nothing else but a

Table 2 Rate constant k_{obs} measured by cyclic voltammetry for the reaction between the radical anion of anthracene and cyclopropylmethyl bromide at different temperatures in 0.1 M Bu_4NBF_4–DMF. Rate constants k_{S_N2} and k_{ET} obtained as $k_{S_N2} = k_{obs} \times \%S_N2$ and $k_{ET} = k_{obs} \times \%ET$

T/°C	k_{obs}/M^{-1} s^{-1}	k_{S_N2}/M^{-1} s^{-1}	k_{ET}/M^{-1} s^{-1}
−50	1.7	0.55	1.15
−40	4.2	1.2	3.0
−30	10	2.7	7.3
−20	21	5.1	15.9
−10	47	11	36
0	100	21	79
10	195	36	159
20	400	72	328
30	670	100	570
40	1230	165	1065

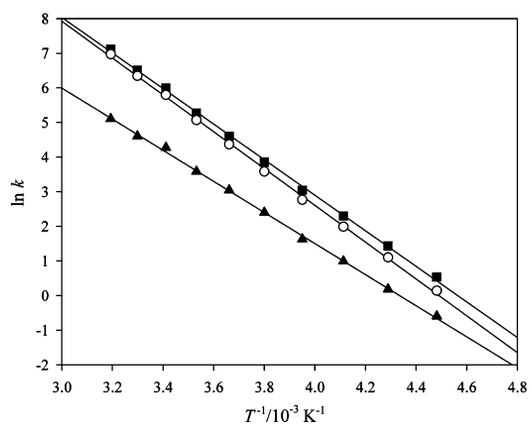


Fig. 2 Arrhenius plots of ln k_{obs} (■), ln k_{ET} (○) and ln k_{S_N2} (▲) *vs.* T^{-1} for the reaction between the radical anion of anthracene and cyclopropylmethyl bromide in 0.1 M Bu_4NBF_4–DMF.

smooth transition in the investigated temperature interval. This also explains why all previously obtained Arrhenius plots for the reactions of radical anions appear linear.[6,31,32] The fact that the pre-exponential factor A according to eqn. (3) is temperature dependent could lead to non-linearity but since the temperature effect on A is much smaller than on the exponential term, $\exp(-E_a/RT)$, of the Arrhenius equations, eqns. (1) and (2), this situation can usually be disregarded.

From the slopes and intercepts of the linear plots in Fig. 2 the following activation parameters are extracted:

S_N2: $E_a^{S_N2} = 37.3$ kJ mol^{-1}, $\Delta H^{\ddagger}_{S_N2}$ (298 K) = 34.8 kJ mol^{-1} and $\Delta S^{\ddagger}_{S_N2}$ (298 K) = −91.4 J mol^{-1} K^{-1}

ET: E_a^{ET} = 44.2 kJ mol^{-1}, $\Delta H^{\ddagger}_{ET}$ (298 K) = 41.8 kJ mol^{-1} and $\Delta S^{\ddagger}_{ET}$ (298 K) = −54.7 J mol^{-1} K^{-1}

Overall: E_a = 42.7 kJ mol^{-1}, $\Delta H^{\ddagger}$ (298 K) = 40.2 kJ mol^{-1} and $\Delta S^{\ddagger}$ (298 K) = −58.3 J mol^{-1} K^{-1}

The experimental uncertainties on the activation enthalpies and entropies are estimated to be 2 kJ mol^{-1} and 10 J mol^{-1} K^{-1}, respectively. If a more realistic value of 3×10^{11} M^{-1} s^{-1} is used rather than ek_BT/h (= 1.7×10^{13} M^{-1} s^{-1}) in the calculations, the activation entropies should be increased by 34 J mol^{-1} K^{-1}.

The main advantage of the present approach is that it makes it possible for the first time to find the activation parameters for two different mechanisms involving the very same reactants. As a comparison of the above numbers reveals, $\Delta H^{\ddagger}_{ET}$ is larger than $\Delta H^{\ddagger}_{S_N2}$ by 7 kJ mol^{-1}, which is attributed to a stronger bonding interaction in the transition state of S_N2. On the other hand, this effect is more than counterbalanced by the fact that the ET mechanism is entropically favoured because of smaller geometrical restrictions. The contribution from the entropy term, $T(\Delta S^{\ddagger}_{ET} - \Delta S^{\ddagger}_{S_N2})$, is 11 kJ mol^{-1} at 298 K as $\Delta S^{\ddagger}_{ET}$ is larger than $\Delta S^{\ddagger}_{S_N2}$ by 37 J mol^{-1} K^{-1}. This is also the reason why the overall (or apparent) values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ determined from the plot of ln k_{obs} *vs.* T^{-1} become relatively close to those extracted for the dominant ET pathway.

It is also interesting to compare these activation entropies with those obtained in previous studies. The activation enthalpies are less useful in this respect, because they are strongly dependent on the exact magnitude of the specific reaction driving force. For the outer-sphere ET reaction between the radical anion of anthracene and the sterically hindered 2-bromo-2-methylpropane or 1-bromoadamantane[31] $\Delta S^{\ddagger}_{ET}$ (298 K) ≈ −40 J mol^{-1} K^{-1}. This value is larger by *ca.* 15 J mol^{-1} K^{-1} than the −54.7 J mol^{-1} K^{-1} obtained herein for the ET reaction involving cyclopropylmethyl bromide. This might be interpreted as if the ET reactions for the less sterically hindered primary substrates have inner-sphere character. Still, the geometrical constraints are not as strong as for the competing S_N2 process with $\Delta S^{\ddagger}_{S_N2}$ (298 K) = −91.4 J mol^{-1} K^{-1}.

It would then be expected that sterically less hindered compounds such as 1-bromobutane and 2-bromooctane should exhibit essentially the same behaviour as cyclopropylmethyl bromide. Their reactions with the radical anion of anthracene do also contain substantial S_N2 components[18,20] of 33 and 8%, respectively, at 298 K, which is close to the 18% found for the S_N2 component herein at 293 K. Indeed, the overall value of $\Delta S^{\ddagger}$ (298 K) measured[31] to −66 J mol^{-1} K^{-1} is relatively close to the present value of −58 J mol^{-1} K^{-1}.

As to the value of $\Delta S^{\ddagger}_{S_N2}$ (298 K) = −91.4 J mol^{-1} K^{-1} obtained for the S_N2 reaction between the radical anion of anthracene and cyclopropylmethyl bromide there are no corresponding literature data available. However, almost the same value of $\Delta S^{\ddagger}_{S_N2}$ (298 K) = −92.9 J mol^{-1} K^{-1} has been found for the S_N2 reaction between the delocalised anion of 4-methoxycarbonyl-1-methyl-1,4-dihydropyridine and 1-bromobutane.[31] Obviously, in these cases there might be an influence originating from differences in the solvation of a radical anion and an anion.§ Finally, it should be mentioned that Marcus[41] on the basis of theoretical considerations has predicted that $\Delta S^{\ddagger}_{ET}$ (298 K) = −40 J mol^{-1} K^{-1} and $\Delta S^{\ddagger}_{S_N2}$ (298 K) = −92 J mol^{-1} K^{-1} in good agreement with the experimental findings.

Product distribution

A closer inspection of the product distributions in Table 1 reveals another interesting feature. As already mentioned the S_N2 mechanism leads to substitution in the 9 position and thus the amount of S_N2 products in this position increases substantially as the temperature is lowered. For the ET mechanism, on the other hand, the substitution takes place in all three positions of 1, 2 and 9. Quite interestingly, positions 9 and 1 seem to become less favored as the temperature is lowered. In other words there is also an entropic influence on the distribution of products formed in the coupling process between the radical anion of anthracene and the butenyl radical. The consequence of these opposing trends for the S_N2 and ET pathways is that the overall distribution of products in the 9, 2 and 1 positions is relatively independent of temperature as shown in Table 3.

§ The entropy for the reduction of anthracene to its radical anion has been determined to be −19 J mol^{-1} K^{-1}.[42] Another study has shown that the influence from the entropy of solvation becomes substantial if the nucleophile is small and with a localised charge. This is presumably the reason why the activation entropy can be as large as −46 J mol^{-1} K^{-1} for the S_N2 reaction between superoxide, $O_2^{\bullet -}$, and benzyl chloride.[43]

Table 3 Molar distribution of the substitution products obtained in the 9, 2 and 1 positions of anthracene in the ET and the (ET + S_N2) reactions between the radical anion of anthracene and three different alkyl halides at $T = 20$ and -40 °C in 0.1 M Bu_4NBF_4–DMF

	$T = 20$ °C		$T = -40$ °C	
Alkyl halide	ET	ET + S_N2	ET	ET + S_N2
Cyclopropylmethyl bromide	1.3 : 1 : 0.3	1.9 : 1 : 0.3	1.1 : 1 : 0.3	2.0 : 1 : 0.3
Bromoethane		4.3 : 1 : 0.5[a]		4.2 : 1 : 0.5
1-Iodoadamantane	4.2 : 1 : 0.3[a]		1.3 : 1 : 0.2	

[a] From ref. 20.

In order to take these investigations a bit further product studies as described in detail in ref. 20 were carried out on the reactions of the radical anion of anthracene with two other substrates, the simple bromoethane and the sterically hindered 1-iodoadamantane, at $T = 20$ and -40 °C, respectively. Although the analysis of the products in these cases cannot be used in a direct quantification of the competition between the two reaction pathways the results still hold important information. As seen in Table 3 the product distribution for the reaction of anthracene radical anion with bromoethane is found to be independent of temperature in accordance with the finding that a competition between S_N2 and ET should also exist for this alkyl halide.[20] On the other hand, the decrease in the amount of 9-substitution for the reaction involving the sterically hindered 1-iodoadamantane is profound as the temperature is lowered because the S_N2 pathway now is completely precluded.[20] The temperature effect on the coupling process between radical anions and alkyl radicals thus appears to be a general feature.

Finally it should be emphasised that a thorough understanding of the origin of the competitive S_N2 and ET pathways would have to rely on detailed molecular dynamics simulations. Recently, the reaction between simple radical anions and methyl halides has been studied by means of *ab initio* calculations.[26–30] One of the main subjects considered in these investigations is the possibility of having inner-sphere ET and S_N2 processes going through the very same transition state and still yielding different products. In the present study we thus cannot exclude that the competition observed in the reaction between anthracene radical anion and cyclopropylmethyl bromide actually is between an outer-sphere ET process on the one hand and an inner-sphere ET/S_N2 process on the other hand. The study also has some consequences with respect to previous measurements of the rate constant for the reaction between $A^{\bullet -}$ and BX. For simple alkyl halides the measured rate constant is $k_{obs} = k_{S_N2} + k_{ET}$ rather than k_{ET} which means that published ratios of k_{sub}/k_{ET} used in the characterisation of substitution reactions should be considered as minimum values.[6] In a forthcoming publication we will show the importance of taking the competition between S_N2 and ET into consideration in the kinetic determination of rate constants for the coupling reaction between radical anions and alkyl radicals.

Experimental

Materials

All chemicals and solvents were of commercial origin unless otherwise noted. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was synthesised according to standard procedures. The solvent *N*,*N*-dimethylformamide (DMF) was dried before use by running it through a column of freshly activated alumina. 9-Cyclopropylmethyl-9,10-dihydroanthracene (**V**) was synthesised by mixing equimoles of 9,10-dihydroanthracene and BuLi (in hexane) in freshly distilled tetrahydrofuran.[44] One equivalent of cyclopropylmethyl bromide was added and after one hour the reaction mixture was quenched with NH_4Cl. The product was extracted twice with diethyl ether and the combined ether phases were washed with water and dried over $MgSO_4$. After removal of the ether *in vacuo*, the purity was checked by GC and ^{1}H NMR. 9,10-Bis(cyclopropylmethyl)-9,10-dihydroanthracene (**VI**) was synthesised as described in the above procedure, replacing 9,10-dihydroanthracene with 9-cyclopropylmethyl-9,10-dihydroanthracene.

Apparatus

Most of the electrochemical equipment was laboratory-built and a description of the experimental set-up and procedures is provided in ref. 31. A conventional potentiostat was employed in the preparative reductions. The product mixtures were quantified using a combination of ^{1}H NMR (Varian 200 MHz) and GC–MS (Hewlett-Packard 6890 GC equipped with an HP-1 column and a Hewlett-Packard 5973 mass selective detector).

NMR

Characteristic ^{1}H NMR data of the substitution products are as follows. 9-(But-3-enyl)-9,10-dihydroanthracene (**I**): δ 3.88 (d, H_{10}, $J = 18.3$ Hz), 3.95 (t, H_9, $J = 6.8$ Hz), 4.15 (d, $H_{10'}$, $J = 18.3$ Hz). 2-(But-3-enyl)-1,2-dihydroanthracene (**III**): δ 6.06 (dd, H_3, $J = 9.4$ Hz, 3.8 Hz), 6.64 (dd, H_4, $J = 9.4$ Hz, 1.7 Hz). 9-Cyclopropylmethyl-9,10-dihydroanthracene (**V**): δ 3.88 (d, H_{10}, $J = 18.6$ Hz), 4.04 (t, H_9, $J = 7.5$ Hz), 4.14 (d, $H_{10'}$, $J = 18.6$ Hz). 9,10-Bis(cyclopropylmethyl)-9,10-dihydroanthracene (**VI**): δ 4.04 (t, H_9 and H_{10}, $J = 7.5$ Hz). The signals pertaining to the products 1-(but-3-enyl)-1,2-dihydroanthracene (**II**) and 9-(but-3-enyl)-10-cyclopropylmethyl-9,10-dihydroanthracene (**IV**) were overlaid by those of the other compounds.

GC and GC–MS

By comparing the integrated ^{1}H NMR signals with the integrated GC signals for three solutions of **V** and **VI** in molar ratios 1 : 3, 1 : 1 and 3 : 1, the response factor of the disubstituted product with respect to the monosubstituted product was determined to be 0.79 ± 0.05. The response factors of different monosubstituted compounds (as well as those of different disubstituted compounds) were assumed to be identical. By running GC samples of known products and product mixtures characterised by ^{1}H NMR the order of retention times was found to be (temperature program: 70 °C for 2 minutes rising to 240 °C with 10 °C min^{-1}; injection temperature: 250 °C): 9-(but-3-enyl)-9,10-dihydroanthracene (**I**), 9-cyclopropylmethyl-9,10-dihydroanthracene (**V**), 1-(but-3-enyl)-1,2-dihydroanthracene (**II**), 2-(but-3-enyl)-1,2-dihydroanthracene (**III**), 9-(but-3-enyl)-10-cyclopropylmethyl-9,10-dihydroanthracene (**IV**) and 9,10-bis(cyclopropylmethyl)-9,10-dihydroanthracene (**VI**).

Procedure

The methodology for measuring rate constants by the cyclic voltammetric technique at different temperatures is described in detail in ref. 31. The preparative reductions were carried out in an ordinary H-cell in 0.1 M Bu_4NBF_4–DMF at a platinum net using a constant potential corresponding to the standard potential of anthracene (= -1.890 V *vs.* SCE). The concentration of anthracene was typically 8 mM and that of cyclo-

propylmethyl bromide 40 mM. Under these conditions the maximal current never exceeded 50 mA. Prior to electrolysis oxygen was removed by purging the solution with argon for 15 minutes. A blanket of argon was maintained on top of the solution throughout the experiment. After electrolysis a few drops of acetic acid were added to the cathode compartment in order to protonate the anions formed. The products were subsequently extracted with diethyl ether. The yield of crude products was 80–90%. The product distribution was quantified using GC on the basis of the retention times and response factors mentioned above. The relative amounts of disubstituted and monosubstituted products varied from experiment to experiment, depending on the concentrations of cyclopropylmethyl bromide and residual water in 0.1 M Bu_4NBF_4–DMF. The reductions were carried out at different temperatures ranging from −50 to 40 °C, at least three times at each temperature. The temperature of the cathode solution was monitored during the reduction by a digital thermometer and adjusted within ±1 °C using either a dry ice–acetone bath or a water bath.

In the preparative experiments, the experimental conditions should be selected to ensure that the ring-closed coupling products would be formed in no other pathways but S_N2. As presented in Scheme 2 these products (**V** and **VI**) might be formed in the ET pathway, if the coupling process between $A^{\bullet -}$ and the cyclopropylmethyl radical is fast compared with the ring-opening of the latter species. In other words, the amount of ring-opened coupling products originating from an ET reaction is dependent on the ratio of the first order rate constant for the ring-opening and the second order rate constant of the coupling process multiplied by $[A^{\bullet -}]$. The rate constant of the coupling process has previously been determined[33,37] in DMF to be about 10^9 M^{-1} s^{-1} while the rate constant for the ring-opening reaction is about 10^8 s^{-1} in THF.[36] It is reasonable to assume that the rate constants are largely independent of solvent, since solvent effects on such reaction types are modest.[45] If the ring-opened product should be favoured in the ET process by a factor of 100 the following restriction is imposed on $[A^{\bullet -}]$, eqn. (7).

$$[A^{\bullet -}] \times 10^9\ M^{-1}\ s^{-1} < 10^8\ s^{-1}/100 \longrightarrow [A^{\bullet -}] < 10^{-3}\ M \quad (7)$$

The formation rate of $A^{\bullet -}$ is directly proportional to the current, while its consumption according to Scheme 2 is determined by its chemical reaction with BX. Under steady-state conditions the following relationship given in eqn. (8) is valid.[37]

$$i/nFV = 2k_{obs}[A^{\bullet -}][BX] \longrightarrow i = 2nFV\,k_{obs}[A^{\bullet -}][BX] \quad (8)$$

Here i denotes the current, n is the number of electrons transferred to the aromatic compound at the electrode, F is the Faraday constant, V is the volume and $k_{obs} = k_{S_N2} + k_{ET}$ denotes the observable rate constant. For $n = 1$, $V = 35$ ml, $k_{obs} = 400\ M^{-1}\ s^{-1}$ (at 20 °C) and [BX] = 0.040 M we find that the restriction outlined in eqn. (7), *i.e.* $[A^{\bullet -}] < 10^{-3}$ M, imposes the following restriction on the current, eqn. (9).

$$i < 108\ A\ (at\ 20\ °C) \quad (9)$$

Obviously, i will never exceed this value under our experimental conditions. At −50 °C, where $k_{obs} = 1.7\ M^{-1}\ s^{-1}$, i should be smaller than 0.46 A on the assumption that the temperature effect on the ring-opening and the coupling process cancels out.

It should be emphasised that the above limits are calculated under the assumption of homogeneous conditions, *i.e.* $A^{\bullet -}$ generated at the electrode diffuses into the solution before reacting with BX. With a reaction half-life of $\ln 2/k_{obs}[BX] = 0.04$ s for [BX] = 40 mM at 20 °C this may seem to present a problem. However, in reality the maximal concentration of $A^{\bullet -}$ in the reaction zone can never exceed the maximal concentration of anthracene used (= 8 mM), so in the worst case 7% of the ET products might be ring-closed compounds. It was found, however, that a lowering of the concentration of anthracene to 1 mM had no effect on the product distribution, thereby precluding this scenario.

References

1 L. Eberson, *Electron Transfer in Organic Chemistry*, Springer-Verlag, Heidelberg, 1987.
2 V. Balzani, Ed., *Electron Transfer in Chemistry*, Wiley, Weinheim, 2001.
3 J. F. Bunnett, *Acc. Chem. Res.*, 1978, **11**, 413.
4 N. Kornblum, *Angew. Chem.*, 1975, **87**, 797.
5 J.-M. Savéant, *Acc. Chem. Res.*, 1980, **13**, 323.
6 H. Lund, K. Daasbjerg, T. Lund and S. U. Pedersen, *Acc. Chem. Res.*, 1995, **28**, 313 and references cited therein.
7 H. Lund and J. Simonet, *J. Electroanal. Chem.*, 1975, **65**, 205.
8 H. Lund and O. Hammerich, Eds., *Organic Electrochemistry*; 4th edn., Marcel Dekker, New York, 2001.
9 C. P. Andrieux, J. M. Dumas-Bouchiat and J.-M. Savéant, *J. Electroanal. Chem.*, 1978, **87**, 39.
10 C. P. Andrieux, J. M. Dumas-Bouchiat and J.-M. Savéant, *J. Electroanal. Chem.*, 1978, **88**, 43.
11 C. P. Andrieux, C. Blocman, J. M. Dumas-Bouchiat and J.-M. Savéant, *J. Am. Chem. Soc.*, 1979, **101**, 3431.
12 C. P. Andrieux, C. Blocman, J. M. Dumas-Bouchiat, F. M'Halla and J.-M. Savéant, *J. Am. Chem. Soc.*, 1980, **102**, 3806.
13 T. B. Christensen and K. Daasbjerg, *Acta Chem. Scand.*, 1997, **51**, 307.
14 R. J. Enemærke, T. B. Christensen, H. Jensen and K. Daasbjerg, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1620.
15 J.-M. Savéant, *J. Am. Chem. Soc.*, 1992, **114**, 10595.
16 H. Jensen and K. Daasbjerg, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1251.
17 F. Maran, D. D. M. Wayner and M. S. Workentin, *Adv. Phys. Org. Chem.*, 2001, **36**, 85.
18 E. Hebert, J. P. Mazaleyrat, Z. Welvart, L. Nadjo and J.-M. Savéant, *Nouv. J. Chim.*, 1985, **9**, 75.
19 K. Daasbjerg and T. B. Christensen, *Acta Chem. Scand.*, 1995, **49**, 128.
20 H. S. Sørensen and K. Daasbjerg, *Acta Chem. Scand.*, 1998, **52**, 51.
21 G. N. Sastry and S. Shaik, *J. Am. Chem. Soc.*, 1995, **117**, 3290.
22 G. N. Sastry, A. C. Reddy and S. Shaik, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1495.
23 G. N. Sastry and S. Shaik, *J. Phys. Chem.*, 1996, **100**, 12241.
24 G. N. Sastry, D. Danovich and S. Shaik, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1098.
25 G. N. Sastry and S. Shaik, *J. Am. Chem. Soc.*, 1998, **120**, 2131.
26 V. Bakken, D. Danovich, S. Shaik and H. B. Schlegel, *J. Am. Chem. Soc.*, 2001, **123**, 130.
27 J. Bertran, I. Gallardo, M. Moreno and J.-M. Savéant, *J. Am. Chem. Soc.*, 1996, **118**, 5737.
28 C. Costentin and J.-M. Savéant, *J. Am. Chem. Soc.*, 2000, **122**, 2329.
29 H. Yamataka, M. Aida and M. Dupuis, *Chem. Phys. Lett.*, 1999, **300**, 583.
30 H. Yamataka, M. Aida and M. Dupuis, *Chem. Phys. Lett.*, 2002, **353**, 310.
31 K. Daasbjerg, S. U. Pedersen and H. Lund, *Acta Chem. Scand.*, 1991, **45**, 424.
32 H. Balslev, K. Daasbjerg and H. Lund, *Acta Chem. Scand.*, 1993, **47**, 1221.
33 S. U. Pedersen and T. Lund, *Acta Chem. Scand.*, 1991, **45**, 397.
34 E. C. Ashby, *Acc. Chem. Res.*, 1988, **21**, 414.
35 M. Newcomb and D. P. Curran, *Acc. Chem. Res.*, 1988, **21**, 206.
36 M. Newcomb, *Tetrahedron*, 1993, **49**, 1151.
37 S. U. Pedersen, T. Lund, K. Daasbjerg, M. Pop, I. Fussing and H. Lund, *Acta Chem. Scand.*, 1998, **52**, 657.
38 D. Occhiallini, S. U. Pedersen and H. Lund, *Acta Chem. Scand.*, 1990, **44**, 715.
39 H. Lund, K. Daasbjerg, D. Ochiallini and S. U. Pedersen, *Russ. J. Electrochem.*, 1995, **31**, 865.
40 S. W. Benson, *Thermochemical Kinetics*, John Wiley & Sons, USA, 1968.
41 R. A. Marcus, *J. Phys. Chem. A*, 1997, **101**, 4072.
42 M. Svaan and V. D. Parker, *Acta Chem. Scand., Ser. B*, 1981, **35**, 559.
43 K. Daasbjerg, PhD thesis, Århus University, Århus, 1993.
44 R. G. Harvey and H. Cho, *J. Am. Chem. Soc.*, 1974, **96**, 2434.
45 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd edn., VCH Verlagsgesellschaft, Weinheim, 1988.