Single Electron Transfer as Rate-Determining Step in an Aliphatic Nucleophilic Substitution

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The rate of transfer of an electron between electrochemically generated anion radicals and alkyl halides has been measured by cyclic voltammetry and the dependence of the rate on the redox potential of the electron donors found. From this dependence, the rate of electron transfer from an electron donor with reorganization energy about 10 kcal mol^{-1} to a given alkyl halide can be calculated if the reversible oxidation potential of the donor is known. The method has been applied to show that the rate of the aliphatic nucleophilic substitution of the enolate ion of 4-methoxycarbonyl-1-methyl-1,4-dihydropyridine on *t*-butyl bromide, neopentyl bromide, and adamantyl bromide is the same as that expected for a SET reaction for a donor with the same oxidation potential as the enolate ion. Primary alkyl halides react somewhat faster than expected for a pure SET reaction. The dianion of dihydroperylene reacts with *t*-butyl chloride and *s*-butyl bromide at the same rate as would be expected for a SET reaction with a donor with the same oxidation potential as the dianion. A model for the aliphatic nucleophilic substitution is discussed.

The classical reaction mechanisms for the aliphatic nucleophilic substitution, S_N1, S_N2 and hybrids of these, have generally been described as involving the transfer of a pair of electrons, pictured by means of the well known curved arrows. During the past twenty years, however, the concept of single electron transfer (SET) has received increased attention.[1-34] Single electron transfer has been suggested to play a role in the aliphatic nucleophilic substitution in several cases. For example, derivatives of *p*-nitrobenzyl, α-nitrohalides, and *gem*-dinitro compounds may react with certain nucleophiles in an $S_{RN}1$ or related reaction.[1-4] In these reactions, the nitro group seems to serve an essential function as a good electron acceptor. The lithium salt of some alkynes reacts with 2-X-2-nitropropane ($X = Cl$ or NO_2) to yield $RC{\equiv}CC(CH_3)_2NO_2$ in a reaction for which a nonchain, electron transfer mechanism ($S_{ET}2$) was considered.[5] Evidence of radicals was obtained in the reaction between 2-butyl *p*-nitrobenzenesulfonate and lithium benzenethiolate in THF. The 2-butyl radical was trapped with phenyl *tert*-butylnitrone and the phenylthio radical detected by the styrene polymerization technique.[6] In the latter two reactions, the nitro group also seems to be essential.

CIDNP has been used as evidence for SET in some reactions between alkyllithium and alkyl iodides.[7-9] The cyclization of 6-iodo-1-hexene,[10] and similar haloalkenes,[11] during the reaction with organolithium compounds has been employed to investigate the importance of free radicals in this reaction. Such a "radical clock" has also been used as argument for the involvment of radicals in the reaction between lithium diisopropylamide and 2,2-dimethyl-1-iodo-5-hexene.[12,13]

EPR spectra and the observation of an unusual substitution product have been used as evidence for SET in the reaction of lithium alkylthiolate and potassium *tert*-butoxide with trityl halides.[12,13] The involvment of SET in the latter reaction has been questioned and an S_N2'-mechanism has been suggested to be responsible for the unusual substitution product.[14] In this connection, it is of interest that the presence of strong bases may

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create some anions, dianions, or substitution products, which may act as electron donors.[15,16] A SET mechanism has been suggested in types of organic and organometallic reactions other than substitution reactions,[17–24] and it is well recognized that the occurrence of radicals during a reaction does not necessarily mean that an observed product is formed through a SET mechanism. Some of the reactions have been questioned or rejected as candidates for a true SET mechanism on the grounds that the rate constant for a SET, calculated, according to Marcus's theory for SET, from thermodynamic data and an estimate of the reorganization energy, λ, was too low compared to the observed reaction rates.[24]

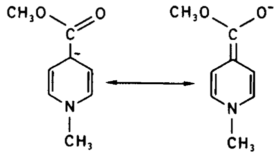
In most investigations, it has been stated or tacitly assumed that SET and S_N2 represent two competing pathways, although a different view has also been presented.[6,25,26] Recently, it has been suggested[27,28] that, in both the S_N2 and SET mechanisms, a single electron shift occurs. The SET pathway involves first a transfer of an electron from the nucleophile to the electrophile followed by bond formation; whereas the S_N2 reaction involves a synchronous shift of a single electron and bond formation.

Anion radicals of aromatic and heteroaromatic compounds have been suggested to react with alkyl halides through an initial transfer of a single electron.[29–33] The stereochemistry of such reactions (inversion vs. racemization) has been interpreted as evidence for a competition between an S_N2 and a SET pathway,[34] with SET being the more important route.

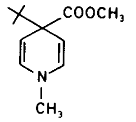
It has been shown previously[26] that the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (*1*$^-$) reacts with *t*-butyl bromide to produce, in high yield, 4-*t*-butyl-1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (*2*) as the only detectable product; that *1*$^-$ is a good SET reagent toward 1,2-dichloro-1,2-diphenylethane; and that the anion of 4-benzoyl-1,4-dihydro-1-methylpyridine is *t*-butylated rather than methylated on reaction with *t*-butyldimethylsulfonium iodide. Reaction of *1*$^-$ with chiral 2-bromooctane gives predominantly racemization together with a small but detectable chirality, probably the result of an inversion.[35] It was suggested[26] that the nucleophilic substitution of *1*$^-$ on *t*-BuBr is a SET reaction, and that the SET reaction and the classical S_N2 reaction are of the same nature, with the SET reaction and S_N2 being extremes of the same model.

In order to accept a SET mechanism, the rate of the reaction must correspond to that expected for a SET.[24] This can be calculated from the Marcus equation when the relevant parameters are known.[36] Another approach is to compare the rate of the nucleophilic substitution reaction with similar reactions for which a SET mechanism is generally accepted. Here, the rate of the substitution reaction of an anion on alkyl halides is compared with the rate of the reaction between aromatic anion radicals and the same alkyl halides.

The enolate anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (*1*$^-$) and the dianion of perylene (*3*$^{2-}$) were investigated as anions, and 2-bromo-2-methylpropane (*t*-BuBr), 2-bromobutane (*s*-BuBr), 1-bromobutane (*n*-BuBr), 2-chloro-2-methylpropane (*t*-BuCl), neopentyl bromide (neoBr), and 1-bromoadamantane (AdBr) used as alkyl halides.



1$^-$



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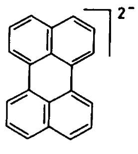


3^{2-}

Results and discussion

Preparative experiments. A prerequisite for discussion of a reaction mechanism is that the product distribution be known. The coupling between *t*-BuBr and electrochemically generated anion

Table 1. Products from the reaction between *t*-butyl bromide and electrochemically generated anion radicals of aromatic A compounds with different redox potentials: E_A/V vs. Ag/0.1 M AgI (E_{NHE}(aq) = $E_{Ag/AgI}$(DMF) −0.35 V.

A	$-E_A$/V	Products (yield/%)[a]	Total yield/%	Total coupling yield/%
4[b]	0.611	*8b*(77), *9b* (12) *10*(3), *4* (5)	97	15
5[b]	0.879	*8a* (50), *9a* (26) *11* (12), *12* (2), *5* (10)	100	40
6[b]	1.200	*13* (66), *14* (10) *15* (10), *6* (0)	86	86
7[c]	1.488	*16* (57), *17a* (26) *17b* (17), *7* (0)	100	100

[a]The yields are average values from 3–5 electrolyses.
[b]Yields determined by HPLC.
[c]Yields determined by GLC.

radicals of pyrene,[37] naphthalene,[38] benzophenone and other aromatic ketones,[39] quinolines and isoquinolines[40] has been described. The two last-named types have also been adamantylated in this way.[41] These anion radicals have, however, relatively low redox potentials, and the expected k_{SET} values are relatively high. So the competition of the SET with other reactions of the anion radical is favourable, and the yield of coupling products high. It was thus of interest to investigate the reaction between *t*-BuBr and anion radicals with less negative reduction potentials in order to elucidate the product distribution and the preparative scope of the coupling reaction.

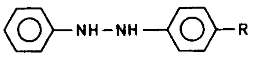
The product distribution was determined by HPLC or GLC and the products identified after isolation. The following compounds were *t*-butylated: 4-methoxycarbonylazobenzene (*4*) ($E = -0.611$ vs. Ag/AgI); azobenzene (*5*) ($E = -0.879$ vs. Ag/AgI); quinoxaline (*6*) ($E = -1.200$ vs. Ag/AgI); and anthracene (*7*) ($E = -1.488$ V vs. Ag/AgI). 4-Methoxycarbonylazobenzene (*4*) gave 77 % 4-methoxycarbonylhydrazobenzene (*8b*), 12 % 1-*t*-butyl-1-(4-methoxycarbonylphenyl)-2-phenylhydrazine (*9b*), and 3 % 1-*t*-butyl-2-(4-methoxycarbonylphenyl)-1-phenylhydrazine (*10*). From *5*, 50 % hydrazobenzene (*8a*), 26 % *N*-*t*-butylhydrazobenzene (*9a*), 12 % 4-*t*-butylhydrazobenzene (*11*), and 2 % 4-*t*-butylazobenzene (*12*) were produced together with 10 % *5*, probably formed by reoxidation of *8a* or *9a* during work-up.

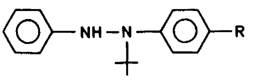
Reductive coupling of *6* with *t*-BuBr yielded 66 % 2-*t*-butyl-1,2-dihydroquinoxaline (*13*), 10 % 2-*t*-butylquinoxaline (*14*), and 10 % 2-*t*-butyl-1,2,3,4-tetrahydroquinoxaline (*15*), and no recovered *6*. This indicated that no 1,4-dihydroquinoxaline formed, since it would have been reoxidized during work-up.

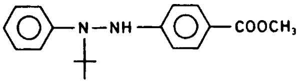
Compound *13* disproportionated to a mixture of *14* and *15*. Pure *13* dissolved in $CDCl_3$ gives, immediately after the solution is prepared, an ^1H NMR spectrum expected of *13*; but after 1–2 h, the signals from *13* disappear and the signals from a 1:1 mixture of *14* and *15* appear. This and the fact that *14* and *15* are formed in equal yield suggest that only *13* is formed during electrolysis; *14* and *15* are formed during work-up by disproportionation of *13*.

Anthracene (*7*) couples reductively and quantitatively with *t*-BuBr to 57 % 9-*t*-butyl-9,10-dihydroanthracene (*16*), 26 % 2-*t*-butyl-1,2-dihydroanthracene (*17a*), and 17 % 1-*t*-butyl-1,2-dihydroanthracene (*17b*). The product distribution of the reductive couplings is given in Table 1.

From Table 1, it is obvious that the more negative the reduction potential the higher the yield of coupling product. The slower the rate of the electron transfer the more time the anion radical has to react in other ways. The most important side reaction is protonation either by residual water or by base-promoted attack on *t*-BuBr, the base being either the anion radical or the hydroxyl ion, which after attack on *t*-BuBr regenerates


8a. R = H
b. R = $COOCH_3$


9a. R = H
b. R = $COOCH_3$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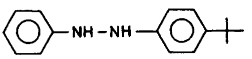
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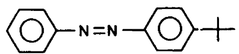
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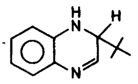
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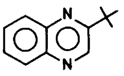
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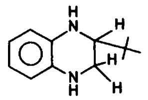
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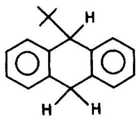
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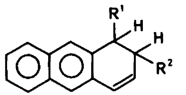

17a. R^1=H R^2=t-Bu *b*. R^1=t-Bu R^2=H

water. *t*-BuBr was shown to be an important source of protons, either directly, or indirectly through reaction with hydroxyl ions, in the reduction of azobenzene. During the reduction of azobenzene, a slow stream of nitrogen was bubbled through the catholyte and the gas produced trapped by cooling to −75 °C. The gas was shown to be 2-methylpropene by its ^{1}H NMR spectrum. Besides $5^{\cdot-}$ and OH^-, $8a^-$ and 11^- may also act as bases in the elimination reaction. This is to be expected in view of the use of *t*-BuCl as a proacid in the reduction of certain heterocyclic compounds where the presence of an acid or high concentrations of strong base are undesirable.

The catalytic reduction of *t*-BuBr is unimportant for the competition between coupling and protonation, so the reaction of the anion radicals with *t*-BuBr can be approximated by the following reactions, (1)–(4), where $A^{\cdot-}$ is the anion radical and BX the alkyl halide:

$$\mathrm{A}^{\cdot-} + \mathrm{BX} \xrightarrow{k_{\mathrm{SET}}} \mathrm{A} + \mathrm{B}^{\cdot} + \mathrm{X}^- \tag{1}$$

$$\mathrm{A}^{\cdot-} + \mathrm{B}^{\cdot} \xrightarrow{\text{fast}} \mathrm{AB}^- \xrightarrow{[\mathrm{H}^+]} \mathrm{ABH} \tag{2}$$

$$\mathrm{A}^{\cdot-} + \mathrm{BX} \xrightarrow{k_{\mathrm{pr}}} \mathrm{AH}^{\cdot} + \mathrm{B(-H)} + \mathrm{X}^- \tag{3}$$

$$\mathrm{AH}^{\cdot} + \mathrm{A}^{\cdot-} \xrightarrow{\text{fast}} \mathrm{A} + \mathrm{AH}^- \xrightarrow{[\mathrm{H}^+]} \mathrm{AH}_2. \tag{4}$$

Assuming the scheme to be essentially correct, the coupling yield is given by:

$$\text{Coupling yield (\%)} = 100\, k_{\mathrm{SET}}/(k_{\mathrm{pr}} + k_{\mathrm{SET}}) \tag{5}$$

$$k_{\mathrm{pr}} = k_{\mathrm{SET}}\,(100/\%\ \text{Yield} - 1). \tag{6}$$

From the measured reaction rate, taken as the sum of k_{pr} and k_{SET}, k_{pr} can be calculated (Table 2). A plot of log k_{pr} dependence on $-E_A$ (vs. Ag/AgI) gives a straight line (Fig. 1):

$$\log k_{\mathrm{pr}} = -5.1 \cdot E_A - 5.5. \tag{7}$$

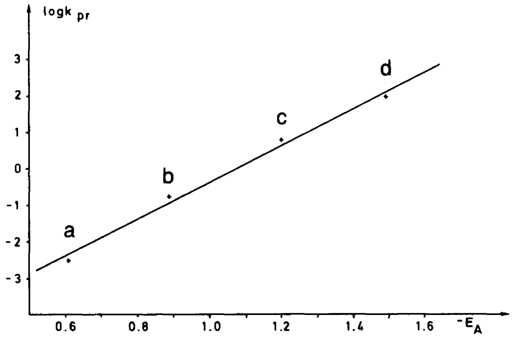
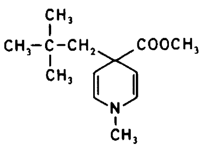


Fig. 1. Rate of protonation, k_{pr}, of aromatic anion radicals in DMF/0.1 M TBAI containing 10^{-2} M *t*-BuBr plotted in relation to the redox potentials of the compounds. (a) 4-Methoxycarbonylazobenzene, (b) azobenzene, (c) quinoxaline, (d) anthracene.

Table 2. Rate of protonation, k_{pr}, of aromatic anion radicals in DMF/0.1 M TBAI containing 10^{-2} M *t*-BuBr.

A-compound	$-E_A$/ V vs. Ag/AgI	k_{SET}/ $mol^{-1}\ s^{-1}$	Coupling yield/ %	k_{pr}[b]/ $mol^{-1}\ s^{-1}$	log k_{pr}
4	0.611	5×10^{-4}[a]	15	3.10^{-3}	−2.52
5	0.879	0.12[a]	40	0.18	−0.74
6	1.200	40	86	6.3	0.80
7	1.488	4.2×10^{-4}	>98	<100	≤2

[a] Calculated from the Marcus equation (see text).
[b] $k_{pr} = k_{SET}[(100/\text{yield}\ (\%))-1]$.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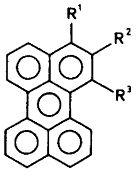
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The rate of the proton abstraction by the anion radical, either from water or *t*-BuBr, is thus proportional to the negative value of the reduction potential of the aromatic compound. Previously, a linear correlation had been found between the anodic peak potential of a series of anions and their pK_A values.[24,43]

The enolate anion $\mathit{1}^-$ has previously been found to make a nucleophilic substitution on *t*-BuBr. Reaction of $\mathit{1}^-$ with neopentyl bromide (neoBr) produced 1,4-dihydro-4-methoxycarbonyl-1-methyl-4-neopentyl-pyridine (*18*) in 85 % yield; on the ^{1}H NMR of the crude product no other products could be seen.

The reaction between the electrogenerated dianion of dihydroperylene (Pe^{2-}) and *t*-BuCl was investigated. The initially formed coupling products, derivatives of dihydroperylene, were oxidized with chloranil to derivatives of perylene. After chromatography, a mixture of three coupling products (*19*, R^1, R^2, or R^3 = *t*-Bu) was isolated in 56 % yield.

Background for test for SET. A critical test for the possibility of a SET mechanism in a nucleophilic substitution reaction is that the rate of the substitution reaction be the same as the rate of the transfer of an electron. The reaction of an aromatic anion radical with an alkyl halide is considered to be a SET reaction,[29–33] and the correctness of this assumption is crucial for the soundness of the arguments in this investigation. Thus, the strategy was to measure the rates of the reactions between a number of anion radicals of aromatic and heteroaromatic compounds with a given alkyl halide. By plotting the observed rate constants against the redox potentials of the compounds, a curve was obtained from which the expected rate of electron transfer from any electron donor to the given alkyl halide could be obtained if the reversible redox potential of the compound is known. We were interested in the reaction of anions and dianions with alkyl halides, the classical nucleophilic substitution reaction. The procedure required that the reversible oxidation potentials of the anion or dianion be known. This is the case for $\mathit{1}^-$[26] and $\mathit{3}^{2-}$.[43] Thus if $E(\mathrm{A}/\mathrm{A}^{\cdot-}) = E(\mathrm{A}_1^{-}/\mathrm{A}_1^{\cdot}) = E(\mathrm{A}_2^{\cdot-}/\mathrm{A}_2^{2-})$ in reactions (8), (9), and (10), and the reorganization energies of the substrate molecules are the same, and the expected k_{SET} is equal to the experimentally observed k_{SUB}, then the substitution reaction will be considered a SET reaction: the transfer of a single electron is the rate-determining step.

$$\mathrm{A}^{\cdot-} + \mathrm{B}_1\mathrm{X} \rightarrow \mathrm{A} + \mathrm{B}_1^{\cdot} + \mathrm{X}^- \tag{8}$$

$$\mathrm{A}_1^{-} + \mathrm{B}_1\mathrm{X} \rightarrow \mathrm{A}_1\mathrm{B}_1 + \mathrm{X}^- \tag{9}$$

$$\mathrm{A}_2^{2-} + \mathrm{B}_1\mathrm{X} \rightarrow \mathrm{A}_2\mathrm{B}_1^{-} + \mathrm{X}^- \tag{10}$$

An underlying assumption for this conclusion is that the Marcus theory for outer-sphere electron transfer is a usable model for these reactions. The use of the Marcus theory in organic chemistry has recently been thoroughly discussed[24,36,45] and only a few points are mentioned below in this connection.

In the Marcus theory, the electron donor and acceptor diffuse together with the rate constant k_d to form an encounter complex in which the electron is transferred, (k_{tr}):

$$A^{\cdot -} + BX \overset{k_d}{\rightleftharpoons} [A^{\cdot -}\cdots BX] \xrightarrow{k_{tr}} A + [BX]^{\cdot -}. \qquad (11)$$

For the electron transfer rate $k_{tr} \ll k_d$, the observed rate k_{obs} is equal to k_{tr}; k_{obs} is dependent on the activation energy for the electron transfer according to

$$k_{obs} = (k_d/A) \cdot \exp(-\Delta G^{\ddagger}/RT). \qquad (12)$$

A is approximately 0.2[45] for the compounds discussed here, and $k_d \sim 2 \cdot 10^{10}$ M^{-1} s^{-1} in acetonitrile at 25 °C.

From this, is obtained

$$\Delta G^{\ddagger} = 1.364\,(11 - \log k_{obs}). \qquad (13)$$

According to Marcus's theory, the activation energy is given by:

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\,(1 + \Delta G^{\circ\prime}/\lambda)^2. \qquad (14)$$

Here λ is the total bond and solvent reorganization energy necessary for the formation of the transition state and $\Delta G^{\circ\prime}$ is derived from ΔG° (the standard free energy) of the reaction by:

$$\Delta G^{\circ\prime} = \Delta G^{\circ} + (Z_1 - Z_2 - 1)\,\frac{N}{4\pi D\varepsilon_0}\,\frac{e^2}{r_{1,2}}; \qquad (15)$$

where Z_1 and Z_2 are the charges of the acceptor and donor, respectively; D the static dielectric constant of the solvent; N Avogadro's number; ε_0 the vacuum permittivity; and $r_{1,2}$ the distance between the acceptor and donor in the encounter complex. For anions and anion radicals, $Z_2 = -1$ and $Z_1 = 0$; so the coulomb contribution vanished. For dianions, this is not strictly correct, but, in an electrolyte solution (0.1 M), the contribution is reduced by a factor ~0.07;[36] in the present case, 2×0.07 kcal mol^{-1}, which is so small compared to other approximations, that it can be neglected. The standard free energy, ΔG°, of the reaction (n = 1) can be obtained from E_A, the redox potential of the donor, and E_{BX}, the redox potential of the acceptor, that is:

$$\Delta G^{\circ} = -F(E_{BX} - E_A). \qquad (16)$$

The bond and solvent reorganization energy, λ, is obtained from:

$$\lambda_{A.BX} = \frac{1}{2}\,(\lambda^{\circ}_{BX} + \lambda^{\circ}_{A}). \qquad (17)$$

λ°_{BX} and λ°_{A} are the total bond and solvent reorganization energies for the so-called self-exchange reaction exemplified by:

$$A + A^{\cdot -} \rightleftharpoons A^{\cdot -} + A;\ \Delta G^{\ddagger}_A = \lambda^{\circ}_A/4. \qquad (18)$$

In equation (17), $\lambda^{\circ}_{BX} \gg \lambda^{\circ}_{A}$; λ°_{BX} is of the order of 100 kcal mol^{-1};[45] whereas $\lambda^{\circ}_{A} \sim 10$ kcal mol^{-1}. The high value of λ°_{BX} is a consequence of the profound changes in the length of the C-X bond during the formation of the transition state, the difference in solvation between the covalently bonded BX and the partly ionic bond in the transition state, and, possibly, minor contributions from changes in the bond angles. For systems where both A and $A^{\cdot -}$ are planar and the charge is delocalized, the changes necessary in going from A (or $A^{\cdot -}$) to the transition state are small. The changes in bond length and bond angles are negligible, and a delocalized charge is less strongly solvated than a localized one.

The λ°_{BX} has not been measured, but has been estimated.[45] The value reported is dependent, of course, on the quality of the data used. However, this was not important in this investigation as it was the transfer from a number of donors to the same BX which was compared. λ°_{A} was obtained for a number of aromatic and heteroaromatic anion radicals and the λ°_{A} was generally 10±2 kcal mol^{-1}. This gives $\lambda_{A.BX}$ for the reaction between $A^{\cdot -}$ and a given BX as:

$$\lambda_{A,BX} = \frac{1}{2}\,(\lambda^{\circ}_{BX} + 10) \pm 1 \text{ kcal mol}^{-1}. \qquad (19)$$

This shows that the variations in $\lambda_{A.BX}$ are relatively small compared to $\lambda_{A.BX}$ as $\lambda_{A.BX} > 50$ kcal mol^{-1}.

Very few values for λ° have been measured for the exchange of an electron between an anion and a radical, $\lambda_{A^{\cdot}.A^{-}}$, and between an anion radical and a dianion, $\lambda_{A^{\cdot-}.A^{2-}}$. For the system $(4\text{-}O_2NC_6H_4)_3C^{\cdot}/(4\text{-}O_2NC_6H_4)_3C^{-}$ $\lambda^\circ = 4{,}3$ kcal mol^{-1} is reported.[45] This system represents a very delocalized one. For a planar anion such as *1*$^{-}$, a slightly higher λ° would be expected. For the exchange between cyclooctatetraene anion radical and the dianion, $\lambda^\circ = 11$ kcal mol^{-1}.[45] On the basis of these very limited data, and general considerations of the factors contributing to λ°, it is assumed that λ° for *1*$^{-}$ and *3*$^{2-}$ is 10±6 kcal mol^{-1}. Therefore, as a first approximation:

$$\lambda_{A^{\cdot-}.BX} \sim \lambda_{A^{-}.BX} \sim \lambda_{A^{2-}.BX} \sim \text{constant.} \tag{20}$$

If the redox potentials for the anion radical and the anion are equal, $E_{A/A^{\cdot-}} = E_{A^{\cdot}/A^{-}}$, and the BX is the same in the reactions considered, then the ΔG° of the reactions are the same. If eqn. (20) is accepted, then eqn. (14) gives:

$$\Delta G^{\ddagger}_{A^{\cdot-}.BX} \sim \Delta G^{\ddagger}_{A^{-}.BX} \sim \Delta G^{\ddagger}_{A^{2-}.BX} \text{ and} \tag{21}$$
$$k_{SUB} \cong k_{A^{-}.BX} \cong k_{A^{2-}.BX} \cong k_{A^{\cdot-}.BX} \cong k_{SET}. \tag{22}$$

Equation (22) is derived on the assumption that the reaction of both the anion and the anion radical with the alkyl halide proceed through a classical nonbonded outer-sphere electron transfer mechanism and that the Marcus equation for the activation energy, $\Delta G^{\ddagger}$, gives an adequate description of the activation energy for such reactions. If k_{SUB} is found different from k_{SET}, one may conclude that the reaction of the anion does not proceed through a pure nonbonded outer-sphere electron transfer mechanism. But how different can the k_{SUB} be from the expected k_{SET} and still consider the reaction a SET?

From the variations in $\lambda^\circ_{A.A^{\cdot-}}$, $\lambda^\circ_{A^{\cdot-}.A^{-}}$, and $\lambda^\circ_{A^{\cdot-}.A^{2-}}$ it is assumed that:

$$\Delta\lambda = \lambda_{A^{\cdot-}.BX} - \lambda_{A^{-}.BX} \sim \pm 3 \text{ kcal mol}^{-1}. \tag{23}$$

Since $\Delta\Delta G^{\ddagger} = 1/4\Delta\lambda$, the rate limits corresponding to the assumption behind eqn. (23) can be calculated (eqn. 24). This means that, if eqn. (24) is fulfilled, the substitution reaction will be considered to be a SET reaction.

$$(1/3.5)\ k_{SET} \le k_{SUB} \le 3.5\ k_{SET}. \tag{24}$$

Kinetic Scheme. Anion radicals of aromatic and heteroaromatic compounds are generally assumed to react with alkyl halides through an initial transfer of a single electron.[29–33] The most important steps are given below as Scheme 1:

Scheme 1.

$$A + e^{-} \rightleftarrows A^{\cdot-} \tag{25}$$

$$A^{\cdot-} + BX \overset{k_{SET}}{\rightleftarrows} A + [BX]^{\cdot-} \tag{26}$$

$$[BX]^{\cdot-} \rightarrow B^{\cdot} + X^{-} \tag{27}$$

$$A^{\cdot-} + B^{\cdot} \xrightarrow{k_2} AB^{-} \tag{28}$$

$$A^{\cdot-} + B^{\cdot} \xrightarrow{k_3} A + B^{-} \tag{29}$$

$$A^{\cdot-} + [H^{+}] \xrightarrow{k_{pr}} AH^{\cdot} \tag{30}$$

$$AH^{\cdot} + e^{-}[A^{\cdot-}] \rightarrow AH^{-} + [A] \tag{31}$$

$$AB^{-}, AH^{-}, B^{-} \xrightarrow{[H^{+}]} ABH, AH_2, BH. \tag{32}$$

The lifetime of $[BX]^{\cdot-}$ is very short. Probably, the electron transfer (26) and the cleavage (27) are synchronous processes. The competition between reactions (28) and (30) has been discussed above on the basis of preparative results as the yield of AH_2 compared to AHB is a measure of the outcome of the competition. The competition between reactions (28) and (29) is discussed below.

In Scheme 1, k_{SET} is the slow step (eqn. 26), as $B^{\cdot}$ is more easily reducible than BX; $k_3 \gg k_{SET}$ as coupling between a radical and an anion radical is a very fast reaction; and, if k_{pr} is much slower than k_2, reaction (30) does not come into play.

A number of other reactions could be included in Scheme 1:

$$AB^{-} + BX \rightarrow AB_2 + X^{-} \tag{33}$$
$$B^{-} + BX \rightarrow B - B \tag{34}$$
$$B^{\cdot} + B^{\cdot} \rightarrow B - B \tag{35}$$
$$B^{\cdot} + HS \rightarrow BH + S^{\cdot} \tag{36}$$
$$B^{\cdot} + A \rightarrow AB^{\cdot} \tag{37}$$

Table 3. Rate of coupling vs. electrocatalytic reduction (k_2/k_3) in the electrochemical alkylation of anion radicals. M_A(f), M_{AH_2} and M_{AX} are the isolated compounds from M_A(b) after the passage of Q_M coulomb (see text).

A	BX	M_A(b)/ mmol	M_A(f)/ mmol	M_{AH_2}/ mmol	M_{AX}/ mmol	Q_M/ C	Q_{corr}/ C	k_{eff}	k_2/k_3
5	*t*-BuBr	0.549	0.060	0.277	0.212	105	51.5	2.53	3.8
6	*t*-BuBr	1.538	0.777	0	0.762	162	162	2.20	9.8
7	*t*-BuBr	0.573	0.008	0	0.565	112	112	2.06	36
7	*n*-BuBr	1.124	0.281	0	0.843	200	200	2.46	4.4

however, these reactions were neglected for the following reasons. No AB_2 coupling products (eq. 33) with BX being a tertiary alkyl halide could be detected by HPLC or MS in any of the preparative reductions. In the reaction between anthracene anion radical ($7^{\cdot-}$) and *t*-BuBr, no $B-B$ (2,2,3,3-tetramethylbutane, eq. (34) and (35), was detected by GLC. Reaction (36) was neglected for tertiary alkyl halides partly because no 2-methylpropane was observed in the reaction between $5^{\cdot-}$ and *t*-BuBr and partly because a tertiary C-H bond is weaker than the C-H bonds in the solvent and supporting electrolyte. Reaction (37) was neglected as the result of the following experiment: *7* was electrolyzed in the presence of *t*-BuBr and naphthalene (5 times the concentration of *7*) at the reduction potential of *7*. Coupling products with anthracene were observed by GLC, but no naphthalene coupling products. This was interpreted to show that the *t*-butyl radical did not attack the aromatic hydrocarbons at a rate comparable to reaction (28), but only coupled with the anion radical (eq. 28).

The competition between the coupling reaction (eq. 28) and the catalytic reduction of BX (eq. 29) was investigated by controlled potential coulometry, using a derivation similar to one developed previously,[46] and assuming Scheme 1 as basis for the kinetics. During the electrolysis, the mass transport to the electrode was the rate determining step, and a steady state approximation could be applied for $A^{\cdot-}$ and $B^{\cdot}$:

$$dB^{\cdot}/dt = dA^{\cdot-}/dt = 0. \tag{38}$$

Using this approximation, the kinetic expression for A can be reduced to:

$$dC_A/dt = -K \cdot p_A \cdot C_A, \tag{39}$$

where $K = 1 - 1/2[1 + k_3/(k_2 + k_3)]$ and p_A is defined by $p_A = m_A \cdot A_e/V$ (m_A is the mass transport to the electrode, A_e the area of the electrode, and V the volume of the catholyte). From $C_A(t) = C_A(0)\exp(-K \cdot p_A \cdot t)$, $i(t) = i(0)\exp(-K \cdot p_A \cdot t)$, and $n_{app} = Q(t)/(F \cdot m_{coup})$[46] eqn. (40) is obtained, where m_{coup} is the number of moles of coupling products formed:

$$k_2/k_3 = 2/(n_{app} - 2). \tag{40}$$

In this derivation, the protonation (eqn. 30) was ignored; (30) can be included from the measurement of the yield of AH_2 in the reaction; and correction for the protonation gives

$$Q_{corr} = Q_{measured} - 2m(AH_2) \cdot F \tag{41}$$

where $m(AH_2)$ is the number of moles AH_2 formed. The results of the coulometric experiments are given in Table 3. It was found that k_2/k_3 increases with increased negativity of E_A, and decreases going from *t*-BuBr to *n*-BuBr.

Cyclic voltammetry (CV) is a useful method for measuring rate constants when the desired reaction rates can be extracted from the measurements by comparison with simulated data. Simulation of CV curves based upon Scheme 1 would be rather complicated so a simplified reaction scheme was used.

Scheme 2.

$$A + e^- \rightleftarrows A^{\cdot-} \tag{25}$$

$$A^{\cdot-} + BX \overset{k_{SET}}{\rightleftarrows} A + B^{\cdot} + X^- \tag{26,27}$$

$$A^{\cdot-} + B^{\cdot} \xrightarrow{\text{fast}} AB^-. \tag{28}$$

The justification for using this simplified scheme is that the coulometric measurements showed that $k_2 > k_3$, and that, in obtaining the results described below, only A compounds, where $k_{SET} \gg k_{pr}$, were employed. That $k_{SET} \ll k_2$ has been argued above. Furthermore, the objective in this investigation was not to find the exact value of k_{SET}, but to show that the rate of the substitution reaction was compatible with a SET mechanism (compare eqn. 24); the approximations made with regard to λ would not justify the small correction of k_{SET} which could result from using a more detailed reaction scheme.

The rate constant k_{SET} was obtained from CV curves by measuring the ratio between the absolute anodic and cathodic peak currents for different concentrations of BX and scan rates v; these ratios were then compared with values obtained by computer simulation of CV curves based on Scheme 2. A description of this is to be published elsewhere.[47] Rate constants from 1 to 1×10^6 M^{-1} s^{-1} can be obtained by this method.

Kinetic results. The results which include k_{SET} for the reactions between a number of anion radicals and *t*-butyl bromide, *s*-butyl bromide, butyl bromide, neopentyl bromide, 1-bromoadamantane, and *t*-butyl chloride in DMF containing 0.1 M $TBABF_4$, and between anion radicals and *t*-butyl bromide in acetonitrile are given in Table 4. The results for *t*-BuBr and *s*-BuBr are also depicted in Fig. 2 and 3. The curves are part of a parabola in accordance with Marcus's theory for outer sphere eletron transfer. The simple alkyl bromides have similar k_{SET} values; whereas, the rate constants for 1-bromoadamantane and neopentyl bromide are significantly lower. The ratio of k_{SET} in DMF and acetonitrile is approximately 2. The k_{SET} for *t*-BuCl is approximately 10^3 times lower than k_{SET} for *t*-BuBr, which would be expected for a SET reaction.

It might be tempting to calculate redox potentials and λ values from the Marcus theory using the part of the parabola (compare Fig. 2 and 3) obtained by plotting log k_{SET} vs. $-E_A$. Reversible redox potentials of alkyl halides cannot be obtained by conventional electrochemical techniques due to the very fast cleavage of $[BX]^{-}$. It has, however, been suggested that a meaningful ΔG (and thus a redox potential for BX) can be defined[45] for the reaction:

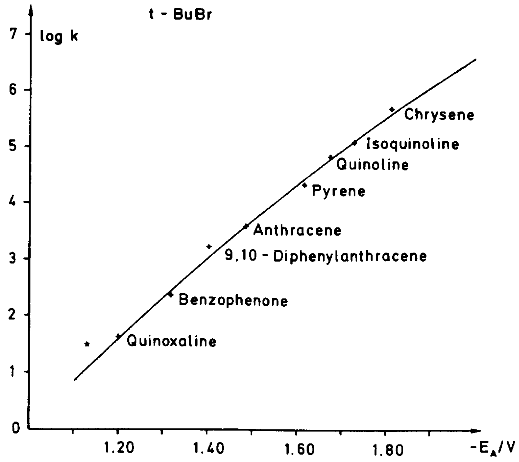

Fig. 2. Rate of electron transfer, k_{SET}, from some electrochemically generated anion radicals (+) and 1^{-}(*) to 2-bromo-2-methylpropane (*t*-BuBr) in DMF/0.1 M $TBABF_4$.

$$BX + e^- \rightarrow B^{\cdot} + X^-,$$

assuming a reduction mechanism in which a simultaneous electron transfer and cleavage are occurring. On that basis, redox potentials for a number of alkyl halides in several solvents have been calculated using thermodynamic data.[45]

Using eqn. (14) ΔG° and λ can be extracted from the data in Table 4 by employing a nonlin-

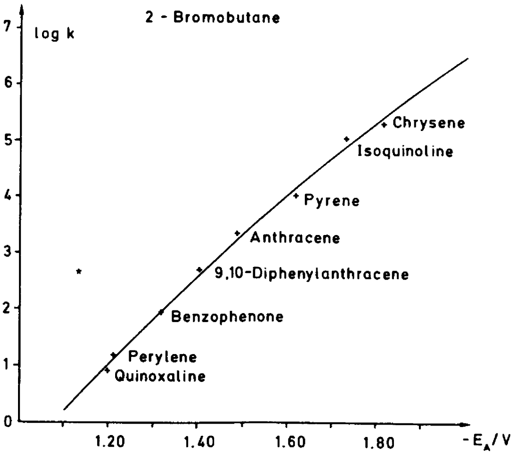

Fig. 3. Rate of electron transfer, k_{SET}, from some electrochemically generated anion radicals (+) and 1^{-}(*) to 2-bromobutane in DMF/0.1 M $TBABF_4$.

Table 4. Rate constants and activation energies for electron transfer from electrochemically generated anion radicals to some alkyl halides in DMF/0.1 M $TBABF_4$ or acetonitrile/0.1 M $TBABF_4$ measured by cyclic voltammetry.

BX	A	$-E_A$/V	k_{SET}/M^{-1} s^{-1}	log k_{SET}	ΔG^{*}/kcal mol^{-1}
Solvent: DMF					
t-BuBr	Quinoxaline	1.200	46	1.66	12.75
–	Benzophenone	1.320	244	2.39	11.74
–	9,10-Diphenylanthracene	1.404	1830	3.26	10.56
–	Anthracene	1.488	4220	3.63	10.05
–	Pyrene	1.618	23900	4.38	9.03
–	Quinoline	1.675	76000	4.88	8.35
–	Isoquinoline	1.731	137000	5.13	8.01
–	Chrysene	1.814	514000	5.73	7.19
s-BuBr	Quinoxaline	1.200	8.0	0.903	13.77
–	Perylene	1.213	16	1.20	13.37
–	Benzophenone	1.320	92	1.96	12.33
–	9,10-Diphenylanthracene	1.404	535	2.73	11.28
–	Anthracene	1.488	2420	3.38	10.39
–	Pyrene	1.618	11500	4.06	9.47
–	Isoquinoline	1.731	119000	5.08	8.07
–	Chrysene	1.814	207000	5.33	7.73
n-BuBr	Quinoxaline	1.200	16	1.20	13.37
–	Perylene	1.213	7.5	0.88	13.80
–	Benzophenone	1.320	92	1.96	12.33
–	Anthracene	1.488	966	2.98	10.94
–	Pyrene	1.618	2455	3.39	10.36
–	Chrysene	1.814	89600	4.95	8.25
EtBr	Perylene	1.213	4.74	0.68	14.08
–	Benzophenone	1.320	40	1.60	12.82
–	Anthracene	1.488	831	2.92	11.02
–	Pyrene	1.618	3290	3.52	10.2
–	Isoquinoline	1.731	37700	4.58	8.76
–	Chrysene	1.814	81000	4.91	8.31
1-AdBr	9,10-Diphenylanthracene	1.404	7.34	0.867	13.82
–	Anthracene	1.488	22.5	1.35	13.16
–	Pyrene	1.618	212	2.33	11.83
–	Chrysene	1.814	10800	4.03	9.51
neoBr	9,10-Diphenylanthracene	1.404	4.34	0.64	14.13
–	Anthracene	1.488	14	1.15	13.44
–	Pyrene	1.618	116	2.06	12.19
–	Chrysene	1.814	3440	3.54	10.18
t-BuCl	Pyrene	1.618	4.67	0.67	14.09
–	Chrysene	1.814	183	2.26	11.92
Solvent: Acetonitrile					
t-BuBr	Quinoxaline	1.200	24	1.38	13.12
–	Benzophenone	1.320	80	1.9	12.41
–	9,10-Diphenylanthracene	1.404	1500	3.16	10.69
–	Anthracene	1.493	2321	3.37	10.41
–	Pyrene	1.636	12845	4.11	9.40
–	Quinoline	1.687	40000	4.60	8.73
–	Isoquinoline	1.734	68000	4.83	8.41
–	Chrysene	1.802	352000	5.55	7.43

ear least-square iteration program in which λ and E_{BX} are the variable parameters.[48] Using such an approach, the following results were obtained [$-E_{BX}$(V vs. NHE), λ(kcal mol^{-1})] in DMF: *t*-BuBr (1.22; 66); *s*-BuBr (1.50; 57); *n*-BuBr (0.88; 82); EtBr (1.41; 63); AdBr (1.76; 56); neoBr (1.48; 69); for *t*-BuBr in acetonitrile (1.25; 66). Much significance should not be placed on these values as they are obtained from a part of the parabola far from the maximum and are thus not dependable. But they could be compared with those obtained from thermodynamic data.[45] E_{BX} for *t*-BuBr in DMF had been calculated as −0.82 V vs. NHE. Recalculation of this value using recently published data for *t*-butyl radical[49] changes this value to −0.94 V vs. NHE. The difference between $E_{t\text{-BuBr}}$ obtained from thermodynamic data and from the Marcus plot (Fig. 2) is thus 0.28 V, which is in acceptable agreement, considering the approximations (for the thermodynamic data especially the transfer enthalpies between water and DMF) made in both approaches. The rather large difference between the potential of the alkyl halides in DMF and acetonitrile suggested by the thermodynamic data[45] could, however, not be substantiated by our experiments. In acetonitrile, $E_{t\text{-BuBr}} = -1.47$ V vs. NHE (using new data[49] −1.59 V vs. NHE) has been calculated.[45] The thermodynamic data give $E_{t\text{-BuBr}}$ (DMF) − $E_{t\text{-BuBr}}$ (AN) = 0.65 V, whereas the experimental difference $E_{t\text{-BuBr}}$ (DMF) −$E_{t\text{-BuBr}}$ (AN) = 0.03 V. The disparity between the calculated and experimental data may be caused by less reliable data available for the solvent transfer energies from water to acetonitrile.

A method is now established for an estimation of k_{SET} from a donor with λ° about 10 kcal mol^{-1} to alkyl halides, when the reversible oxidation potential of the donor is known. A reaction between an anion, A^-, and an alkyl halide can be described by:

$$A^- + BX \rightarrow [A^\cdot + B^\cdot + X^-] \rightarrow AB + X^-. \quad (42)$$

The enolate anion, *1*$^-$, was obtained from *1*$^+$ in two reversible one-electron reductions. Considering the reversible reduction of the stable radical *1*$^\cdot$ to *1*$^-$ as the E step, the following sequence can be described as a classical EC reaction:

$$A^\cdot + e^- \rightleftharpoons A^- \quad (43)$$

$$A^- + BX \xrightarrow{k_{SUB}} AB + X^-, \quad (44)$$

and k_{SUB} calculated from case VI in Ref. 50 from the ratio of the anodic and cathodic peaks in the cyclic voltammograms of the second peak in the reduction of *1*$^+$ in the presence of different concentrations of BX.

The reaction rates of the substitution reactions of *1*$^-$ on several alkyl halides are reported in Table 5, in which the ratio of k_{SUB}:k_{SET} is also tabulated. The expected k_{SET} was obtained from Fig. 2 and 3 and analogous curves for the other alkyl halides. It was found that the observed rate of the reaction between *1*$^-$ and *t*-BuBr, AdBr, and neoBr agreed within a factor of 2 with the rate expected for a SET reaction for these alkyl halides. As no products are found other than the substitution products (eqn. 44), and the rate of substitution thus was the same as the rate of a SET reaction, it is highly probable that *the rate-limiting step in the aliphatic nucleophilic substitution of the enolate ion* 1$^-$ *on* t-*butyl bromide, neopentyl bromide and 1-adamantyl bromide is the transfer of a single electron.* The reaction rates of *s*-BuBr, *n*-BuBr, and EtBr were higher than the expected SET reaction. This means that the substitution was not a pure outer-sphere electron transfer reaction.

The reaction of a dianion follows a similar pattern as an anion. The substitution would thus be:

$$A^{2-} + BX \rightarrow [A^{\cdot-} + B^\cdot + X^-] \rightarrow AB^- + X^-. \quad (45)$$

In a system where A^{2-} is formed through two reversible one electron reductions of A, the second reduction, followed by eqn. (45), can be regarded as an EC reaction and the rate of the chemical step calculated in a known manner[50] from the anodic and cathodic peak currents in the presence of BX.

In Table 6, the rates of the reactions between the dianion of dihydroperylene, (*3*$^{2-}$), and *t*-BuCl and *s*-BuBr, and between the dianion of anthrahydroquinone and *s*-BuBr are given. The ratios of the observed rates to the expected k_{SET} are also included. The results strongly suggest that the substitution reactions between *3*$^{2-}$ and the two alkyl halides have the transfer of a single electron as rate-determining step, whereas the reaction involving the dianion of anthrahydroquinone is somewhat faster than expected for a pure SET reaction.

Table 5. The rate of substitution of the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (1^-) on some alkyl halides in DMF/0.1 M $TBABF_4$. AdBr = 1-bromoadamantane, neoBr = 1-bromo-2,2-dimethylpropane, neopentylbromide.

A	BX	E_2^0/V^a	$k_{SUB}/M^{-1}\cdot s^{-1}$	$k_{SET}/M^{-1}\cdot s^{-1}$	k_{SUB}/k_{SET}
1-Methyl-4-methoxy-carbonylpyridinium iodide	AdBr	−1.13	$1.5\cdot10^{-2b}$	$1.9\cdot10^{-2}$	0.80
–	neoBr	–	$2.9\cdot10^{-2b}$	$2.3\cdot10^{-2}$	1.3
–	*t*-BuBr	–	30^c	12	2.5
–	*s*-BuBr	–	480^c	2.8	170
–	*n*-BuBr	–	1420^c	3.5	400
–	EtBr	–	3052^c	1.2	2500

[a]Measured against the Ag/AgI, $I^- = 0.10$ M reference electrode.
[b]Obtained by polarography.
[c]Obtained by cyclic voltammetry.

Table 6. The rate of substitution of the dianions of dihydroperylene and anthrahydroquinone on some alkyl halides in DMF/0.1 M $TBABF_4$.

A	BX	E_2/V^a	$k_{SUB}/M^{-1}\cdot s^{-1}$	$k_{SET}/M^{-1}\cdot s^{-1}$	k_{SUB}/k_{SET}
Perylene	*t*-BuCl	−1.80	171^b	141	1.21
Perylene	*s*-BuBr	−1.80	$950\cdot10^{3b}$	$211\cdot10^{3}$	4.5
Anthraquinone	*s*-BuBr	−1.123	48	2.2	22

[a]Measured against Ag/AgI, $I^- = 0.10$ M.
[b]Obtained by cyclic voltammetry.

Discussion

As mentioned above, it has been suggested previously[6,25,26] that the SET reaction and the classical S_N2 reaction were of the same nature, the SET and S_N2 reactions being extremes of the same model. Recently, the polar reaction-SET dichotomy in nucleophilic substitution has been discussed[27,28] in terms of single electron shift and timing of the bond formation between the resulting radicals. This investigation demonstrates that the reaction between a resonance-stabilized enolate ion such as 1^- and sterically hindered alkyl halides (*t*-BuBr, neoBr, and AdBr) proceeds as a "pure" SET reaction with negligible bond formation between the nucleophile and electrophile in the transition state. 1^- Transfers the electron to the antibonding orbital of BX with formation of $1^\cdot$ and $B^\cdot$ ($+X^-$). Since $1^\cdot$ is stable, it does not dimerize as in the oxidation of many anions. A close approach of the bulky 1^- to the central carbon atom of BX before the electron transfer is made difficult in the sterically hindered alkyl halides. Only after electron transfer and loss of halide ion, do the bond angles change and the bulky groups allow a closer approach with resulting bond formation. The secondary and especially the primary halides allow a closer approach in the transition state. The substitution rates found are 400–2200 times faster than the SET. This corresponds to a stabilization of the transition state, relative to a pure SET transition state, of 3–5 kcal mol^{-1}. If this stabilization is caused by the beginning of a bond formation, the bond is much weaker than would be expected for the bonds in a "classical" S_N2 transition state. The formation of such a weak bond in the transition state would explain the inversion of configuration for a small part of the molecules together with the predominant racemization found for secondary alkyl halides in such reactions.[34,35] If the model is correct, it should not be necessary to explain this outcome as a result of a competition between two different pathways, S_N2 and SET.

The very bulky nucleophile, 3^{2-}, reacted even with *s*-BuBr at the same rate as anion radicals. This was interpreted to show that the approach of 3^{2-} to *s*–BuBr in the transition state is not close enough to stabilize it significantly by bond formation. The dianion of anthrahydroquinone, where the charge is more localized on oxygen, reacted somewhat faster than expected for SET. The results are thus compatible with a model for the aliphatic nucleophilic substitution where the transfer of an electron and bond formation may be nonconcerted or concerted, or a hybrid of these in the transition state, and parameters such as oxidation potential of the nucleophile, reduction potential of the electrophile, steric hindrance, solvent, and temperature play a rôle in determining where, on this spectrum of possible transition states, a given reaction will have its transition state. Quite generally, nucleophiles with high oxidation potentials ("hard" nucleophiles) require much stabilization by bond formation in the transition state (TS), as found in the classical S_N2 transition state; whereas, nucleophiles with low oxidation potential ("soft" nucleophiles) have a TS closer to the pure SET TS.

If it is possible to view SET and S_N2 as two extremes of a model, what about S_N1? If the S_N1 reaction is included in the model, it would be from the fact that the carbocation formed as an intermediate in the S_N1 reaction is a much better electron acceptor than the alkyl halide, and the rôle of this carbocation is to make it possible to transfer an electron, possibly in concert with a bond formation. It remains to be seen whether such an extension of the model is useful.

The common nucleophiles have oxidation potentials so much more positive than the reduction potentials of the common electrophiles that a pure outer-sphere electron transfer is an extremely slow reaction, and a concerted, or very nearly concerted, electron transfer and bond formation are to be expected. Experimental evidence for the involvement of SET can thus be expected only for very easily oxidized nucleophiles or very easily reduced electrophiles.

Experimental

Materials. 4-Methoxycarbonylazobenzene was prepared through the acid chloride of 4-phenylazobenzoic acid.[51] 4-Methoxycarbonyl-1-methylpyridinium iodide was obtained by quaternization of methyl isonicotinoate with methyl iodide in acetonitrile. The other compounds were commercially available and purified when necessary. Analytical grades of tetrabutylammonium iodide (TBAI) and DMF were obtained from Fluka AG, Switzerland. Tetrabutylammonium fluoborate ($TBABF_4$) was prepared from TBABr and $NaBF_4$ in water, and recrystallized from water and acetonitrile/diethyl ether.

Instrumentation. The apparatus used for cyclic voltammetry was constructed at the Department of Chemistry, University of Aarhus, and will be described elsewhere.[52] The polarograph was a Polariter PO4, Radiometer, Copenhagen. The HPLC analyses were performed with a 30 cm RP18 column, flow 1 ml/min. GLC was performed with a Hewlett-Packard 5790 gas chromatograph with an OV-1 column: injection temperature 250 °C; 100 °C for 4 min; to 230 °C at 9 °C/min.

Procedure. Kinetic CV experiments. A thermostated cell ($t = 25 \pm 0.2$ °C) containing 10 ml DMF/0.1 M $TBABF_4$ was used. The DMF/$TBABF_4$ was dried over molecular sieves (4Å) and passed once or twice through a column of alumina (Woelm W200 neutral). The alumina had been dried by heating to 450 °C in vacuum (0.1 Torr) for 20 h. A HME, on a platinum disc with area 0.8 mm^2, was used as working electrode, a mercury pool as counterelectrode, and potentials measured against a comparison electrode, a silver wire in DMF/$TBABF_4$ separated from the cell solution.[53] The potential was checked after each experiment by adding anthraquinone and measuring the peak potentials. The peak potential of the first peak of anthraquinone was measured against ferrocene.[54] The solution resistance was compensated for by using a positive feedback device.[52] The potential of $E_{Ag/AgI} = E_{NHE}(aq) + 0.35$ V.

The concentrations of the A compounds, *1*, and *3* were 2 mM. The ratios between the anodic and cathodic peak currents were measured for 3–5 different concentrations of alkyl halide. For every addition of BX, the ratios were obtained for 4–5 scan rates. By comparison of these ratios with computer-simulated values[47] or literature data,[50] the rate constants could be obtained. The percent standard deviations for the rate constants ranged from 5 to 20.

Kinetic polarographic experiments. The reactions between 1^- and AdBr and neoBr were too slow for the CV experiments, so the disappearance of 1^- in the reactions was followed by polarography directly in the solution. 200 Mg of 1^+ in 55 ml DMF/TBAI was reduced to 1^- at −1.4 V (Ag/AgI). When the reduction was completed (15 min.), the slow background decay (due to a slow protonation by solvent and/or supporting electrolyte) of 1^- was followed for some time by recording the anodic current at −0.6 V. Carefully deaerated neoBr (1.5 ml) was then added and the concentration of 1^- followed. When all 1^- had decayed, 200 mg 1^+ were added and reduced, and the disappearance of 1^- followed. The rate constants for the two experiments agreed within 5 %.

Preparative experiments. The electrolyses were performed in DMF/0.1 M TBAI at room temperature with a mercury pool as cathode and Ag/AgI as reference electrode. Nitrogen was bubbled slowly through the solution during the reduction. The aromatic compound was reduced in the presence of 5 to 10 times molar excess of alkyl halide. After the electrolysis, water was added to the catholyte and the products extracted with diethyl ether, washed twice with water, dried and evaporated. The product mixture was analyzed by HPLC and/or GLC, the products separated by column chromatography or preparative TLC and identified by conventional means. The yields are given in Table 1. The relative deviation between the electrolyses in a series may be 10 %.

Reduction of azobenzene and t-*BuBr.* Reduction potential −0.90 V vs. Ag/AgI. Products analyzed by HPLC with anthracene as internal standard, 85 % methanol 15 % water as eluent, UV detector at 260 nm. Isolated were azobenzene, hydrazobenzene, and the two following *t*-butylated compounds: 4-*t*-butylazobenzene (*12*), ^{1}H NMR ($CDCl_3$) δ 1.39 (s, 9H), 7.43–7.59 (m, 5H), 7.78–7.96 (m, 4H), ^{13}C NMR ($CDCl_3$) δ 39.0, 42.7, 130.3, 130.5, 133.7, 136.8, 138.4, 158.4, 160.6, 162.3; N-*t*-butylhydrazobenzene (*9a*), ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 9H), 5.7 (s, 1H), 6.60–7.27 (m, 5H), 7.3 ("s", 5H), ^{13}C NMR ($CDCl_3$) δ 34.7, 66.6, 120.6, 126.3, 132.7, 134.0, 136.0, 136.6, 156.2, 157.1.

4-*t*-Butylhydrazobenzene (*11*) was observed in HPLC, but was oxidized to *12* during work-up. If oxygen was bubbled through the solution analyzed by HPLC, the peak corresponding to *11* disappeared and the peak of *12* grew.

Reduction of 4-methoxycarbonylazobenzene (*4*). Reduction potential −0.75 V (Ag/AgI). For HPLC, stilbene was internal standard, eluent 85 % methanol 15 % water, detector at 300 nm. The following butylated compounds were isolated: 1-*t*-butyl-1-(4-methoxycarbonylphenyl)-2-phenylhydrazine (*9b*), ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 9H), 3.86 (s, 3H), 6.11 (s, 1H), 7.25 ("s", 5H), 6.86–6.97 (m, 2H), 7.77–7.90 (m, 2H), (The "singlet" is the signal from 2-phenyl group; a N-*t*-butyl group neighbour to the phenyl ring causes the phenyl multiplet to be broader.); 1-*t*-butyl-2-(4-methoxycarbonylphenyl)-1-phenylhydrazine, ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 9H), 3.82 (s, 3H), 5.7 (s, 1H), 6.5–7.0 (m, 2H), 7.10–7.25 (m, 5H), 7.76–7.96 (m, 2H).

Reduction of quinoxaline (*6*) *and* t-*BuBr.* Reduction potential −1.3 V (Ag/AgI), internal standard for HPLC 2-hydroxyquinoline, eluent 75 % methanol 25 % water. Isolated were: 2-*t*-butyl-1,2-dihydroquinoxaline, *13,* ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 9H), 3.70 (deform. t, 1H, $J \sim 2.6$ Hz), 3.95 (br.s, 1H), 6.3–7.2 (m, 4H), 7.4 (deform. t, 1H, $J \sim 2.6$ Hz), IR (KBr) cm^{-1} 3310 (s), 3215 (w), 3190 (w), 2950 (s), 1610 (s), 1515 (m), 1490 (s), 1475 (m), 1385 (m), 1315 (s), 1295 (w), 1120 (m), 1015 (w), 745 (s), (In $CDCl_3$ solution, *13* disproportionates into *14* and *15*.); 2-*t*-butylquinoxaline (*14*), ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 9H), 7.5–8.2 (m, 4H), 8.93 (s, 1H), IR (KBr) cm^{-1} 2980 (m), 1565 (m), 1505 (m), 1490 (m), 1478 (m), 1110 (ms), 1030 (w), 975 (m), 780 (s), MS (*m/e,* %) 187 (6), 186 (59), 172 (29), 171 (100), 144 (40); 2-*t*-butyl-1,2,3,4-tetrahydroquinoxaline (*15*), m.p. 84 °C, ^{1}H NMR ($CDCl_3$) δ 0.91 (s, 9H), 2.9–3.4 (m, 3H), 3.45 (s, 2H), 6.4 (s, 4H), IR (KBr) cm^{-1} 3350 (s), 2800–3000 (m), 1590 (m), 1505 (s), 1495 (s), 1450 (m), 1290 (s), 1120 (m), 730 (s), MS (*m/e,* %) 191 (11), 190 (78), 134 (27), 133 (100), 132 (29), 92 (20).

Reduction of 1^+ *and neoBr.* Reduction potential −1.20 V (Ag/AgI). In the ^{1}H NMR spectrum of the crude product, besides some neoBr, only 1,4-dihydro-4-methoxycarbonyl-1-methyl-4-neopentylpyridine could be detected. The compound was purified on a column of silica with dichloromethane as eluent. ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 9H), 1.67 (s, 2H), 2.90 (s, 3H), 3.69 (s, 3H), 4.6 (d, 2H, *J* 8.1 Hz), 5.8 (d, 2H, *J* 8.1 Hz). MS (*m/e*, %): 224 (MH^+, 4), 166 (13), 165 (42), 164 (100), 153 (26), 152 (92), 108 (42), 107 (54), 106 (35), 93 (24), 57 (19).

Reduction of anthracene and t-*BuBr.* Reduction potential −1.6 V (Ag/AgI), the reaction mixture (coupling products, yield ~100 %) was analyzed by GLC; isomer ratio 57:26:17 for 9-*t*-butyl:2-*t*-butyl:1-*t*-butyldihydroanthracene. The isomers were identified from a 300 MHz ^{1}H NMR spectrum of the isomer mixture. ^{1}H NMR ($CDCl_3$):

9-*t*-Butyl-9,10-dihydroanthracene (*16*), δ 0.90 (s, 9H), 3.62 (s, H_9), 3.70 (d, H_{10}, $^2J_{10\,10'}$ 18.78 Hz), 4.14 (d, $H_{10'}$, $^2J_{10'10}$ 18.80 Hz), 7.1–7.7 (m, 8H);

2-*t*-Butyl-1,2-dihydroanthracene (17a), δ 0.87 (s, 9H), 2.20–2.27 (m, H_2), 2.80 (octet, H_1, $^2J_{11'}$ 15.14 Hz, $^2J_{12}$ 10.26 Hz, $^4J_{19}$ 1.17 Hz), 2.95 (q, $H_{1'}$, $^3J_{1'1}$ 15.14 Hz, $^3J_{1'2}$ 7.03 Hz), 6.05 (q, H_3, $^3J_{34}$ 9.87 Hz, $^3J_{32}$ 3.42 Hz), 6.61 (q, H_4, $^3J_{43}$ = 9.88 Hz, $^4J_{42}$ 2.55 Hz); 7.1–7.7 (m, 6H);

1-*t*-Butyl-1,2-dihydroanthracene (*17b*), δ 0.85 (s, 9H), 2.45–2.60 (m, H_2, $H_{2'}$) 2.6–2.72 (m, H_1), 5.93 (octet, H_3, $^3J_{34}$ 9.50 Hz, $^3J_{32}$ 6.3 Hz, $^3J_{32'}$ 2.5 Hz), 6.47 (octet, H_4, $^3J_{43}$ 9.46 Hz, $^4J_{42}$ 2.50 Hz, $^4J_{42'}$ ~0.9 Hz); 7.1–7.7 (m, 6H).

Reduction of perylene and t-*BuCl.* Reduction potential −1.80 V. 1.00 g of perylene was reduced in the presence of *t*-BuCl (5 ml) in 180 ml DMF/TBAI. After the reduction, 3.0 g of chloranil were added to oxidize the dihydroperylenes to perylene derivatives. After 8 h, the DMF solution was poured into water and extracted with dichloromethane. After removal of the dichloromethane, the residue was separated on a column of silica with dichloromethane as eluent. 800 Mg (56 %) of coupling products were isolated. Three isomers of *t*-butylperylene were found with one isomer being the major product, ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 9H), 7.33–7.72 (m, 6H), 8.0–8.4 (m, 5H). The *t*-butyl signals from the two other isomers were at δ 1.56 and δ 1.49. MS (*m/e*, %) 309 (15), 308 (59), 274 (15), 293 (64), 276 (20), 253 (24), 252 (100), 250 (20), 138 (13), 132 (12), 126 (15).

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