

On the Occurrence of Electron Transfer in Aliphatic Nucleophilic Substitution

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Three types of evidence, the activation entropy and enthalpy based on temperature measurements, stereochemical results based on preparative electrolysis, and $k_{\text{SUB}}/k_{\text{ET}}$ values based on kinetic measurements give the picture that sterically very hindered alkyl halides react with aromatic anion radicals and certain anions in an outer-sphere electron transfer, whereas a certain stabilization of the transition state is found when the steric hindrance is diminished. The activation entropies and activation enthalpies for the reactions between aromatic anion radicals or the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine ($\mathbf{1}^-$) and alkyl halides have been calculated from the temperature dependence of the rate constants. A relatively small negative activation entropy and relatively high activation enthalpy is found for the reactions with sterically hindered alkyl halides, whereas reactions with less hindered alkyl halides have more negative activation entropies and lower activation enthalpies. These properties change gradually through the series as the steric hindrance for an $\text{S}_{\text{N}}2$ reaction changes. The change in activation parameters in a series occurs sooner for $\mathbf{1}^-$ than for the aromatic anion radicals.

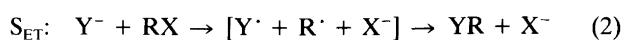
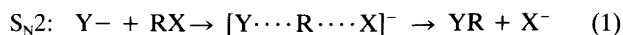
The role of electron transfer (ET) in aliphatic nucleophilic substitution has been the subject of investigation for the last two decades. The problem has been addressed both theoretically and experimentally.^{1–10} The main questions have been whether an electron transfer was at all possible as a step in a nucleophilic substitution reaction (S_{ET}) and, if so, whether there existed a sequence of reactions in which the characteristics of the $\text{S}_{\text{N}}2$ reaction gradually changed to those of an S_{ET} reaction in a somewhat similar way to that suggested for the transition between the polar reactions $\text{S}_{\text{N}}2$ – $\text{S}_{\text{N}}1$.

A typical $\text{S}_{\text{N}}2$ reaction [eqn. (1)] is, as is well known, characterized by a backside attack on the central carbon atom by the nucleophile, requiring a geometrically well defined transition state and a relatively strong bonding in the transition state between the central carbon atom and both the attacking nucleophile and the leaving group. A typical reaction of this type is the Finkelstein reaction, e.g. ethyl chloride reacting with chloride ion. The $\text{S}_{\text{N}}2$ reaction has also been described as an inner-sphere (or bonded) electron transfer by analogy with certain inorganic reactions;¹¹ another way of describing the reaction is as an electron shift synchronous with bond formation.⁸

The characterization of electron transfer reactions should be based on physically measurable properties such as the stereochemical outcome of a reaction, activation parameters (ΔH^\ddagger , ΔS^\ddagger), and relative kinetic rates (e.g. $k_{\text{SUB}}/k_{\text{ET}}$). This principle leads to the classification of organic ET reactions into three groups. One type is outer-sphere ET reactions; the term outer-sphere (non-bonded)

ET will be used in the conventional way to describe an adiabatic ET reaction in which the stabilization of the transition state due to coupling is small, usually taken to be less than 1 kcal mol⁻¹. The term inner-sphere (bonded) ET reaction is also used conventionally to describe a reaction in which there is substantial bonding stabilization in the transition state. In between these groups is a 'grey' area in which the characteristics of an outer-sphere ET reaction are gradually replaced by those of an inner-sphere ET reaction. The 'grey zone' will be defined as the part of the inner-sphere region in which the bonding stabilization of the transition state is not large enough to determine decisively the stereochemistry of the product.

An S_{ET} reaction [eqn. (2)] involving an outer-sphere (non-bonded) ET would be expected to have a less strictly defined geometry in the transition state and no bonding between the central carbon atom and the attacking and leaving nucleophiles. A reaction which comes close to these characteristics is the substitution of the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine ($\mathbf{1}^-$) on bornyl bromide. The $\text{S}_{\text{N}}2$ and S_{ET} reactions may be formulated as shown in eqns. (1) and (2).



The problems have previously been addressed in different ways. Attempts have been made to observe directly by ESR or CIDNP the radicals which according to eqn. (2)

should be formed as transients in the reaction; radicals have been observed in the reaction between alkyllithium compounds and some alkyl iodides.^{9,10}

In another strategy, an electron transfer was shown to be made energetically plausible either by using thermodynamic data⁶ or by comparing the rate of the nucleophilic substitution (k_{SUB}) with the rate of the reaction (k_{ET}) of the alkyl halide with an electron donor which is supposed to be an outer-sphere electron donor and which has the same oxidation potential and approximately the same reorganization energy as the nucleophile.⁴ Aromatic anion radicals have been used as outer-sphere electron donors in such investigations. A ratio $k_{\text{SUB}}/k_{\text{ET}}$ of ca. 1 would then be characteristic of an S_{ET} reaction.

The stereochemical outcome of such reactions has been investigated both for the reaction between aromatic anion radicals^{5,12} and alkyl halides and for 1^- and some alkyl halides.¹³ The reaction between aromatic anion radicals and alkyl halides results mostly in a racemization or *exo/endo* isomerization, although in some cases a small amount of inversion has been observed for a secondary halide.⁵ A recent report suggests^{6c} on theoretical grounds that the reaction is not a pure outer-sphere electron transfer, but that an inner-sphere component is present in the transition state; however, this component does not, according to the report, influence the stereochemistry of the product. In the reaction between 1^- and bornyl and isobornyl bromide a nearly total *exo/endo* isomerization was observed.¹³

The steric requirement of an $S_{\text{N}}2$ reaction compared with that of an S_{ET} reaction would be expected to result in a more negative activation entropy compared with that of an S_{ET} reaction; on the other hand, the activation enthalpy of an $S_{\text{N}}2$ step would be expected to be lower than that of an S_{ET} owing to the bonding stabilization in the $S_{\text{N}}2$ transition state compared with the much weaker bonding in the S_{ET} transition state. Indeed, this has been shown to be the case for the transition state in the reaction between anthracene anion radical and the three butyl bromides at room temperature.¹⁴

In this investigation the dependence on the temperature of the rate of the reaction (rate constant k_1) between a number of aromatic anion radicals and some alkyl bromides and of the reaction between 1^- and the same alkyl halides was measured, and the results used to obtain the values for the activation entropies and activation enthalpies of the reactions. The alkyl bromides employed were the three butyl bromides, *exo*-norbornyl bromide, bornyl bromide, and 1-bromoadamantane, and the nucleophiles/electron donors were 1^- and the anion radicals of pyrene, anthracene, benzophenone, quinoxaline, and perylene.

Results

The rate constants were measured in DMF in the temperature interval -50 to 50°C either by cyclic voltammetry (CV)¹⁵ or, for the slow reactions, by use of a rotating

disc electrode or an ultramicroelectrode to follow the homogeneous kinetics.¹⁶

For the rate measurements by CV the ratio between the anodic peak current $i_{\text{p,a}}$ measured relative to the baseline and the cathodic peak current $i_{\text{p,c}}$ was measured at 3–5 different sweep rates, v , in the interval $-0.36 < i_{\text{p,a}}/i_{\text{p,c}} < -0.10$. At each scan rate the average value of $i_{\text{p,a}}/i_{\text{p,c}}$ was measured from three experiments. The rate constant k_1 could then be calculated by combining the experimental parameters v , the concentration of the electron donor $[A]_0$, and the ratio of the concentration of the electrophile $[RX]_0$ to $[A]_0$ with the measured ratio $i_{\text{p,a}}/i_{\text{p,c}}$. The uncertainty of the measured value of k_1 is estimated to be 10%. The CV experiments were repeated at least twice for every temperature with new solutions and electrodes.

A rotating glassy carbon electrode or ultramicroelectrode was used to monitor the decay of the concentration of the anion radical after addition of the alkyl halide. The aromatic compound (1–5 mM) was reduced preparatively at a platinum foil electrode or a mercury pool electrode in a conventional H-cell. The solution was stirred for 2–5 s after addition of an at least a tenfold excess of the alkyl halide. The exponential decay of the anodic current of the anion radical was recorded for 2–4 half-lives on a digital oscilloscope. Twenty to forty data points were selected automatically and a linear least-squares test of the logarithm of the current versus time was made giving the slope and the correlation coefficient. The latter value was always better than 0.99. The slope of the straight line corresponds to $-2k_1[RX]_0$ for the aromatic anion radicals and for 1^- to $-k_{\text{SUB}}[EX]_0$. The experiments were repeated 2–3 times at each temperature.

Linear sweep voltammetry (LSV) was attempted for the rate measurements, but was abandoned as the results showed large fluctuations, especially at low temperatures where a large excess of the alkyl halide had to be used to obtain a measureable increase in the peak height. Some direct reduction of the RX may have taken place when high concentrations of RX were used, but other factors may also play a role.

The dependence of the natural logarithm of the rate constant k_1 on T^{-1} should be linear according to the Arrhenius equation $k_1 = A \exp(-E_A/RT)$ and from the slope the activation energy may be obtained. The activation enthalpy and activation entropy may be calculated from eqns. (3) and (4).¹⁷

$$\Delta H_{\ddagger}^{\ddagger} = E_A - RT \quad (3)$$

$$\begin{aligned} \Delta S_{\ddagger}^{\ddagger} &= 2.303 R [\log k_1 - \log(ek/h) - \log T] + E_A T^{-1} \\ &= 4.576 (\log k_1 - 10.75 - \log T) + E_A T^{-1} \end{aligned} \quad (4)$$

E_A is in cal mol^{-1} ; k and h are Boltzmann's and Planck's constants, respectively.

The type of data obtained by these methods is illustrated in Fig. 1 and Table 1, which gives the results from the

Table 1. Rate constants k_{ET} at different temperatures for the reaction between anthracene anion radical and butyl bromide.

T/K	$T^{-1}/10^{-3} K^{-1}$	$k_{ET}/M^{-1} s^{-1}$	$\ln k_{ET}$
213.2	4.690	0.92 ^a	-0.08
223.2	4.480	2.20 ^a	0.79
223.4	4.476	2.74 ^b	1.01
233.2	4.288	6.58 ^b	1.88
233.2	4.288	6.80 ^a	1.92
243.0	4.115	15.2 ^b	2.72
253.4	3.946	33.9 ^b	3.52
263.3	3.798	70.4 ^b	4.25
273.2	3.660	136.2 ^b	4.91
283.5	3.527	256.6 ^b	5.55
295.3	3.386	507 ^b	6.23
303.2	3.298	773 ^b	6.65
313.2	3.193	1289 ^b	7.16
323.6	3.090	2169 ^b	7.68

^aMeasured by following the disappearance of $A^{\cdot-}$ using a rotating disc electrode or ultramicroelectrode. ^bMeasured by CV.

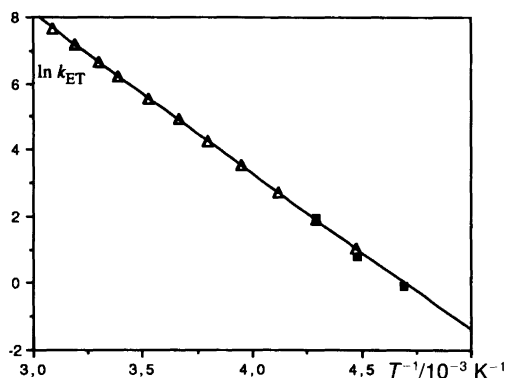


Fig. 1. Temperature dependence of the rate constants of the reaction between anthracene anion radical and butyl bromide in DMF/TBABF₄ obtained by cyclic voltammetry (Δ) or homogeneous kinetic measurements using a rotating disc electrode (\blacksquare).

Table 2. Activation enthalpy ΔH_{298}^\ddagger and activation entropy ΔS_{298}^\ddagger for reactions between some alkyl halides and some electron donors/nucleophiles.

RX	A	$-E_A^\circ/V^c$	$\Delta H_{298}^\ddagger/kcal mol^{-1}$	$\Delta S_{298}^\ddagger/cal mol^{-1} K^{-1}$
Butyl bromide	Pyrene	1.592	8.43	-14.9
	Anthracene	1.488	8.93	-15.8
	Benzophenone	1.296	10.16	-16.8
	Perylene	1.189	11.57	-17.5
	Quinoxaline	1.175	11.11	-17.1
	1^-	1.130	6.25	-22.2
sec-Butyl bromide	Pyrene	1.592	7.30	-16.6
	Anthracene	1.488	8.05	-17.0
	Benzophenone	1.296	10.29	-15.8
	Perylene	1.189	10.71	-17.9
	Quinoxaline	1.175	11.46	-15.4
	1^-	1.130	7.55	-19.8
1^-^a	1.130	7.17	-22.5	
tert-Butyl bromide	Pyrene	1.592	8.52	-10.4
	Anthracene	1.488	9.50	-10.7
	Benzophenone	1.296	12.76	-6.6
	Perylene	1.189	12.74	-7.5
	Quinoxaline	1.175	13.51	-6.9
	1^-^a	1.130	11.12	-15.8
exo-Norbornyl bromide	Pyrene	1.592	9.50	-11.9
	Anthracene	1.488	10.94	-11.0
	Benzophenone	1.296	13.75	-9.6
	$1^-^{a,b}$	1.130	13.23	-16.2
1-Bromoadamantane	Pyrene	1.592	11.50	-9.2
	Anthracene	1.488	13.04	-8.6
	Benzophenone ^{a,b}	1.296	16.70	-5.0
	$1^-^{a,b}$	1.130	17.60	-9.4
Bornyl bromide	Pyrene	1.592	11.19	-9.1
	Anthracene	1.488	11.98	-11.0
	Benzophenone ^{a,b}	1.296	16.18	-6.0
	$1^-^{a,b}$	1.130	17.19	-8.9

^a[$A^{\cdot-}$] measured using a rotating disc electrode. ^b[$A^{\cdot-}$] measured using an ultramicroelectrode. The other rate constants obtained using CV. ^c vs. Ag/AgI, 0.1 M I⁻. The uncertainty of ΔH_{298}^\ddagger is estimated to be $\pm 0.5 kcal mol^{-1}$ and for ΔS_{298}^\ddagger $\pm 2 cal mol^{-1} K^{-1}$.

reaction between anthracene anion radical and butyl bromide using CV and homogeneous kinetic measurements. As the two methods give results which are situated on the same straight line the confidence in the data is strengthened. As is seen from Fig. 1 a plot of $\ln k_1$ vs T^{-1} gives a straight line, in contrast with published data,¹⁴ and similar straight lines were obtained in all cases; in no case was a break in the line observed. The data used to construct Fig. 1 are given in Table 1.

Discussion

The linear dependence of $\ln k_1$ on T^{-1} shown in Fig. 1 indicates that there is no change in the mechanism with temperature in the interval -50 to 50°C for the reaction of anthracene anion radical with butyl bromide. As a linear dependence of $\ln k_1$ on T^{-1} was observed in all the cases (24 reactions, Table 2) for anion radicals (and also for $\mathbf{1}^-$, six reactions) it is reasonable to assume that this would be found for other reactions of aromatic anion radicals with alkyl halides.

The values for the activation enthalpy ΔH_{298}^\ddagger and the activation entropy ΔS_{298}^\ddagger for a number of combinations of electron donors and alkyl halides are shown in Table 2. In Table 3 the values of $\Delta S_{298,A}^\ddagger$ for the reactions between the aromatic anion radicals and the alkyl halides are compared with the values of $\Delta S_{298,1^-}^\ddagger$ for the reaction between $\mathbf{1}^-$ and the same alkyl halides. In the second column the values of $\Delta S_{298,A}^\ddagger$ for a given alkyl halide is obtained as the average of the values of the alkyl halides given in Table 2, as it is assumed that the transition states for a given alkyl halide and the different anion radicals have approximately the same steric congestion and thus similar ΔS_{298}^\ddagger values, which also is borne out by the experimental results.

The values of $\Delta S_{298,A}^\ddagger$ for the reaction between aromatic anion radicals and alkyl halides show an interesting trend. The sterically less hindered halides, butyl and *sec*-butyl bromides, have a relatively large (numerically) negative value ($-16.5 \text{ cal mol}^{-1} \text{ K}^{-1}$) whereas the sterically more hindered halides (*tert*-butyl bromide, *exo*-norbornyl bromide, bornyl bromide, and 1-bromoadamantane) have less negative activation entropies (-7.6 to $-10.8 \text{ cal mol}^{-1} \text{ K}^{-1}$).

Table 3. Some activation parameters from the reactions between aromatic anion radicals or $\mathbf{1}^-$ with alkyl halides. ΔS^\ddagger in $\text{cal mol}^{-1} \text{ K}^{-1}$ and $\Delta\Delta G_{\Delta S}^\ddagger$ in kcal mol^{-1} .

Alkyl halide	$\Delta S_{298,A}^\ddagger$	$\Delta S_{298,1^-}^\ddagger$	$\Delta\Delta G_{\Delta S}^\ddagger$
Butyl bromide	-16.4	-22.2	4.0
<i>sec</i> -Butyl bromide	-16.5	-21.2	3.7
<i>tert</i> -Butyl bromide	-8.4	-15.8	2.2
<i>exo</i> -Norbornyl bromide	-10.8	-16.2	1.6
1-Bromoadamantane	-7.6	-9.4	0.5
Bornyl bromide	-8.7	-8.9	0.1

Table 4. Differences in activation enthalpy between the reaction of an alkyl halide with an anion radical with the same oxidation potential as $\mathbf{1}^-$ ($\Delta H_{298,A}^\ddagger$) and $\mathbf{1}^-$ ($\Delta H_{298,1^-}^\ddagger$).

Alkyl halide	$\Delta H_{298,A}^\ddagger$	$\Delta H_{298,1^-}^\ddagger$	$\Delta\Delta H_{298,A,1^-}^\ddagger$	$k_{\text{SUB}}/k_{\text{ET}}$
Butyl bromide	12.0	6.3	5.7	400
<i>sec</i> -Butyl bromide	11.6	7.4	4.2	170
<i>tert</i> -Butyl bromide	13.4	11.1	2.3	2.5
<i>exo</i> -Norbornyl bromide	15.4	13.2	2.2	1.7
1-Bromoadamantane	18.2	17.6	0.6	0.3
Bornyl bromide	17.7	17.2	0.5	0.2

A likely interpretation is that the transition state for butyl and *sec*-butyl bromides requires a more defined stereochemistry than the sterically more hindered alkyl halides, and that this is an indication of weak bonding between the anion radical and the alkyl halide in the transition state. The reaction between aromatic anion radicals and these two halides (and presumably also for other sterically less hindered alkyl halides) seems thus not to be a pure outer-sphere electron transfer, but has some inner-sphere electron transfer character, in agreement with Ref. 6(c).

The sterically hindered alkyl halides have approximately the same, less negative, activation entropy, and this points to these reactions being of the outer-sphere electron transfer type. It seems thus permissible to use such reactions as standards for reactions in which the rate-determining step is suspected to be the transfer of an electron and where no substantial bonding stabilization of the transition state is found.

The reactions between the anion radicals and butyl and *sec*-butyl bromides are thus not reliable standards for outer-sphere electron transfer reactions, and the values for $k_{\text{SUB}}/k_{\text{ET}}$ previously reported are thus too low for these compounds because the measured rate constant k_{ET} does not correspond to a pure outer-sphere ET.

The reactions between the enolate ion $\mathbf{1}^-$ and the alkyl halides show a similar trend, but for $\mathbf{1}^-$ the reactions may be divided into three groups. The reactions of $\mathbf{1}^-$ with the sterically very hindered halides (bornyl bromide and 1-bromoadamantane) have an activation entropy similar to that of the corresponding reactions of these halides with the anion radicals, and the reaction thus probably involves an outer-sphere electron transfer. The reactions of $\mathbf{1}^-$ with alkyl halides in the second group (butyl and *sec*-butyl bromides) have significantly more negative activation entropies. A third group (*tert*-butyl bromide and *exo*-norbornyl bromide) with activation entropies between these two groups consists of alkyl halides which have some steric hindrance but less than, e.g., bornyl bromide. The reactions in this group thus seem to involve some bonding stabilization in the transition state, but less than the second group.

If it is accepted that the activation entropy found for the reaction between *tert*-butyl bromide, *exo*-norbornyl

bromide, 1-bromoadamantane, or bornyl bromide and aromatic anion radicals (about $-8.9 \text{ cal mol}^{-1} \text{ K}^{-1}$) is the activation entropy to be expected for an outer-sphere reaction of this type and which is mainly due to solvent properties, then the difference at 298 K: $\Delta\Delta G_{298,\Delta S}^\ddagger = 298(\Delta S_{298,A}^\ddagger - \Delta S_{298,1^-}^\ddagger)$ would indicate the increase in activation energy due to the change in activation entropy compared with an outer-sphere electron transfer reaction. The results are shown in column 4 in Table 3.

These results may be compared with the stereochemical outcome of the reactions. The reaction between 1^- and bornyl and *isobornyl* bromides yielded nearly the same mixture of *exo*- and *endo*-products, which indicated the transient existence of a bornyl radical and thus an outer-sphere electron transfer reaction. The reaction between 1^- and the *exo*- and *endo*-norbornyl bromides also gave both the *exo*- and *endo*-products, but the ratio (about 1:3 and 30:1) was not the same from the *exo*- and the *endo*-norbornyl bromides. This again indicates that although some *exolendo* isomerization takes place a certain inner-sphere component is found in the transition state. The stereochemical evidence and the results from the measurements of the activation entropy thus point to the same conclusion.

The activation enthalpy for the reaction between an electron donor with the same oxidation potential as 1^- and the alkyl bromides may be obtained by using the equation $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. A comparison of the values of the activation enthalpies for the reactions between aromatic anion radicals with the alkyl halides with that of the reaction between 1^- and the same alkyl halides may be made by extrapolating the experimental values for $\Delta G_{298,A}^\ddagger$ to the redox potential of 1^- and using the average values of $\Delta S_{298,A}^\ddagger$ from Table 3 to calculate the $\Delta H_{298,A}^\ddagger$ corresponding to the redox potential of 1^- . In Table 4 the thus calculated

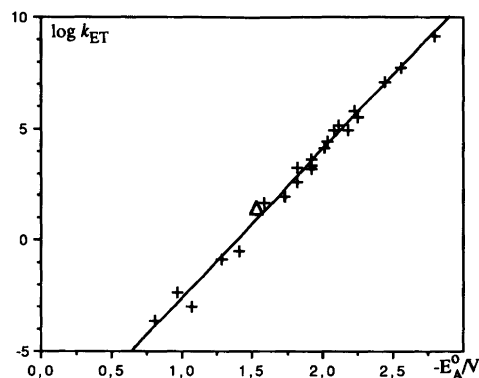


Fig. 2. Logarithm of the rate of reaction ($\log k_{ET}$) in DMF between *tert*-butyl bromide and aromatic anion radicals (+) or 1^- (Δ) vs. $-E_A^0$ (SCE).

$\Delta H_{298,A}^\ddagger$ and $\Delta H_{298,1^-}^\ddagger$ are listed together with the difference $\Delta\Delta H_{298,A,1^-}^\ddagger = \Delta H_{298,A}^\ddagger - \Delta H_{298,1^-}^\ddagger$. The previously published values for k_{SUB}/k_{ET} are listed in column 5.

Even though the Marcus theory predicts a parabolic relationship between $\Delta G_{298,A}^\ddagger$ and the standard potentials of the donors the extrapolation of the experimental values for $\Delta G_{298,A}^\ddagger$ to the redox potential of 1^- was carried out by linear least-squares analysis. This decision is in accordance with some very convincing experimental results presented in Fig. 2, where the rate of electron transfer to *tert*-butyl bromide from a series of aromatic anion radicals is shown; the fastest reactions ($k_{ET} > 10^7 \text{ M}^{-1} \text{ s}^{-1}$) are measured by pulse radiolysis¹⁸ the others by electrochemical methods^{4b,19} (cyclic voltammetry, or homogeneous kinetics using a rotating disc electrode as an indicator electrode). Together the range of rate constants spans 13 orders of magnitude, and Fig. 2 indicates a linear correlation between the oxidation potential of the donor (including 1^-) and the

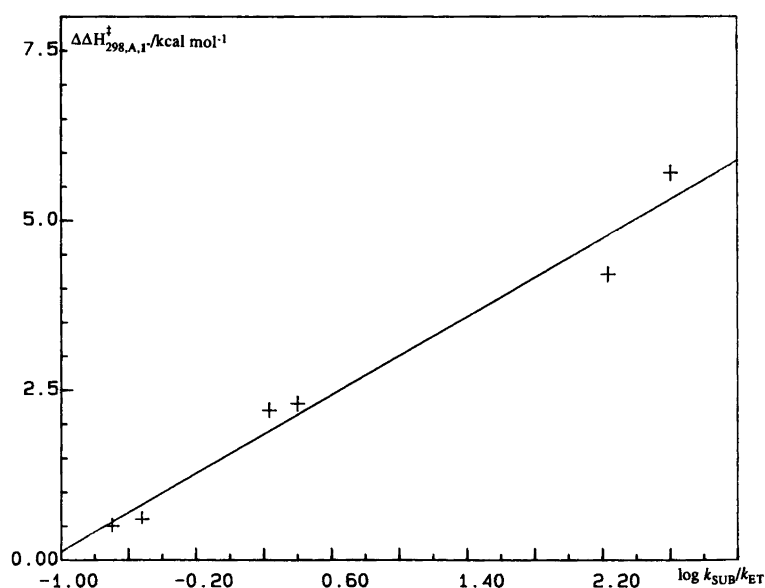


Fig. 3. Correlation between $\Delta\Delta H_{298,A,1^-}^\ddagger$ (see the text) and $\log k_{SUB}/k_{ET}$.

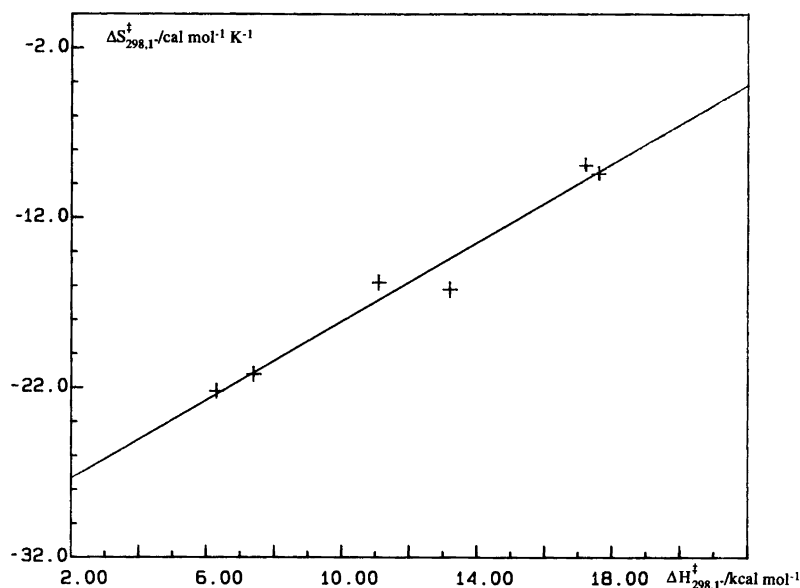


Fig. 4. Correlation between $\Delta S_{298,1}^{\ddagger}$ and $\Delta H_{298,1}^{\ddagger}$ for the reaction between 1^- and alkyl halides in DMF/TBABF₄.

logarithm of the rate of electron transfer to the electrophile and thus also a linear $\Delta G^{\ddagger}/E_A^{\circ}$ relationship; these results thus indicate that the theories²⁰ that predict a quadratic correlation between ΔG^{\ddagger} and the driving force require some amendment when applied²¹ to dissociative electron transfer reactions.

From the columns 4 and 5 in Table 4 it is seen that $\Delta\Delta H_{298,A^{\cdot-},1}^{\ddagger}$ and $k_{\text{SUB}}/k_{\text{ET}}$ follow the same trend; actually, a plot of $\Delta\Delta H_{298,A^{\cdot-},1}^{\ddagger}$ vs. $\log(k_{\text{SUB}}/k_{\text{ET}})$ gives a straight line (Fig. 3). It is gratifying that the experimental results from the temperature measurements and the measurements of the rate constants⁴ give the same picture of the reaction between 1^- and alkyl halides.

A plot of $\Delta S_{298,1}^{\ddagger}$ vs. $\Delta H_{298,1}^{\ddagger}$ gives a straight line (Fig. 4). It is to be expected that $\Delta H_{298,1}^{\ddagger}$ increases when $\Delta S_{298,1}^{\ddagger}$ decreases numerically on going to more sterically hindered alkyl halides where a non-bonded ET is assumed to occur, but it might be fortuitous that a linear connection is observed.

It may thus be concluded that the three types of evidence, the activation entropy and enthalpy based on temperature measurements, the stereochemical results based on preparative electrolysis, and the $k_{\text{SUB}}/k_{\text{ET}}$ values based on kinetic measurements give the same picture: the sterically very hindered alkyl halides react with aromatic anion radicals and 1^- in an outer-sphere electron transfer reaction; when the steric hindrance becomes smaller a certain stabilization of the transition state is found. The S_N2 character increases in a series of alkyl halides sooner for 1^- than for the anion radicals for a given change in steric hindrance. However, for all the reactions studied here the stabilization of the transition state is considerably smaller than for the transition state of a typical S_N2 reaction. The results are thus consistent with the hypothesis that there exists a series of aliphatic nucleophilic substitution reac-

tions in which the characteristics of an S_N2 reaction are gradually replaced by the characteristics of an S_{ET} reaction. Of course, it may be defined that all ET reactions which are not outer-sphere ET are inner-sphere ET reactions, but the inclusion of a 'grey zone' illustrates that all properties do not change abruptly at a transition state stabilization of 1 kcal mol⁻¹ from the characteristics of an outer-sphere ET to those of an inner-sphere reaction. In such an interpretation attention is focussed on average properties and not the fate of a single molecule, which, e.g., stereochemically has to react either with retention or inversion.

Another conclusion from the experiments is that the reaction between anion radicals and sterically less hindered alkyl halides is not a pure outer-sphere ET, but has certain inner-sphere character.

Experimental

Materials. Bornyl bromide²² and *exo*-norbornyl bromide²³ were prepared according to the references given. HBr was prepared according to Ref. 24. The other alkyl bromides were obtained commercially and were, like the supporting electrolyte Bu₄NBF₄ and the solvent *N,N*-dimethylformamide (DMF), purified by standard procedures. Before each experiment the electrolyte solution was dried by passage through a column of activated alumina.

Instrumentation. The potentiostat and recording system have been described elsewhere.¹⁵ The platinum disc ultramicroelectrode of diameter 10 μm was prepared according to the instructions in Ref. 25. The electrode was polished with diamond paste (0.25 μm). The rotating disc electrode used was a platinum electrode of diameter 3 mm. The comparison electrode was a silver wire in Bu₄NBF₄/DMF; potentials were checked afterwards against the redox po-

tential of anthraquinone. The temperature was measured with a NiCr–Ni temperature probe, which was connected to an IMPO PT-200 digital thermometer. The probe was put inside a glass tube with methanol, which was immersed in the cathode compartment. The temperature could be controlled to a certain value in the interval -50 to $+50$ °C with an accuracy of ± 0.5 °C.

Procedure. Measurement of the k_1 rate constants by CV were performed by the method described by Pedersen and Svensmark.¹⁵ The cell was thermostatted by being immersed in a Dewar flask containing water (0–50 °C) or methanol (–50–0 °C). Values of k_1 less than $10 \text{ M}^{-1} \text{ s}^{-1}$ were measured by means of a potentiostatic method using an ultramicroelectrode or a rotating disc electrode following the procedure described in Ref. 16.

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