Degree of Electron Transfer in Some Nucleophilic Reactions Determined by Activation Parameters

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Activation parameters have been measured from the temperature dependence of rate constants for a number of reactions between, on the one hand, electron donors such as aromatic anion radicals and nucleophiles such as the anions of 4-methoxy-carbonyl-1,4-dihydro-1-methylpyridinium and 4-benzoyl-1,4-dihydro-1-methyl-pyridinium, and, on the other hand, different kinds of electrophile such as benzyl halides and vicinal dichlorides. For the sterically very hindered substrates the same activation enthalpy and entropy is found in the nucleophilic substitutions and reductive eliminations as in the electron transfer (ET) reactions with the anion radicals indicating that ET is the rate-determining step in these cases. When the electron-donating ability of the anion or the steric hindrance of the substrate is diminished the values of the activation parameters become smaller reflecting increasing stabilization of the transition state and thus a change of mechanism towards the more polar reactions (S_N2 and E2). Even in the ET reactions between aromatic anion radicals and the less sterically hindered benzyl halides a certain inner-sphere character seems to be present. These conclusions are in accordance with those previously drawn from kinetic measurements. The results are compared with activation parameters for similar reactions reported in the literature.

During the last two decades a major topic for study in physical organic chemistry has been the borderline between classical polar reactions (S_N2, E2), where electron transfer and bond formation are concerted, and electron transfer reactions, where an initial rate-determining electron transfer (ET) without significant bond formation is followed by fast reactions, e.g., coupling or reduction as shown in Scheme 1, where Nu is the nucleophile, X and Y are halogen atoms, and S_{ET} and E_{ET} stand for substitution-ET and elimination-ET, respectively. One of the issues that has been discussed is whether, for a given reaction, the polar mechanism and ET are truly competing pathways, or whether the reaction is rather characterized merely be a certain degree of electron transfer. The latter viewpoint suggests that through a series of similar reactions one could find a gradual change from reactions with 'pure' ET characteristics to a reaction with more polar character. This question has been addressed both stereo-chemically,[1] kinetically[2] and thermodynamically.[3]

A distinction between a polar and an ET pathway for a given reaction must be based on chemical or physicochemical experiments, the outcome of which in the present case is determined by the transition state (TS) of the reaction. The TS of an ET-type reaction differs in two important ways from the TS of its polar counterpart.

(1) In the polar reaction, be it S_N2 or E2, there is a very well defined geometry associated with the TS. In the S_N2

S_{ET}:
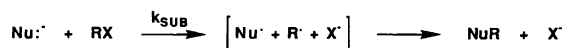
E_{ET}:
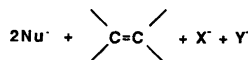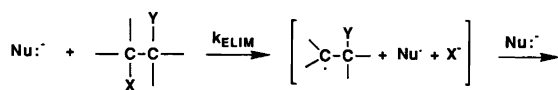
Scheme 1.

reaction the nucleophile has to attack from the backside of the central carbon atom, while the E2 elimination can be viewed as an attack by Nu on the X in the X–C bond,[4] where X denotes the more electropositive of the atoms X and Y. In this respect the TS of the E2 reaction is similar to the TS of the S_N2 reaction. In the 'pure' outer-sphere ET reaction, on the other hand, the restrictions on the TS geometry are much less severe, as there has only to be a certain overlap between the HOMO of the nucleophile and the LUMO of the substrate, and this overlap can be

attained by several different orientations of the reactants in TS.

(2) In a polar reaction bond breaking and bond formation take place to a large extent in the TS, whereas the TS of an outer-sphere ET reaction is void of bond formation. (Usually the term outer-sphere ET is applied to reactions where the stabilization of the TS due to bond formation is less than 1 kcal mol^{-1}).[5]

These differences in the characteristics of the TS in polar and a non-polar reaction pathways make it possible to distinguish between the two by applying various types of experiment.

Product analysis. In the reactions that are the subject of the current investigation the product distribution is kinetically controlled, and hence the product distribution reflects the energy of the TS of the reaction. In the S_N2 reaction the backside attack of the nucleophile on the central carbon atom leads to inversion. If, on the other hand, the reaction proceeds through radical intermediates, as in the ET reaction, the stereochemical identity is lost during the reaction. Indeed the degree of racemization vs. inversion has been shown to correlate well with the degree of ET character in some nucleophilic substitution reactions.[1c,d]

In a polar reductive elimination (Red-E2) with the two leaving groups X and Y the favoured conformation in the TS is the antiperiplanar configuration (*syn*-elimination is mostly found in systems where the steric hindrance is prohibitive for the *anti*-configuration).[4] An elimination of a *meso* (or *erythro*) compound therefore gives the *E*-alkene exclusively, whereas a ± (or *threo*) compound will yield the *Z*-alkene. Extensive experimental evidence supports this conclusion.[4] In an elimination initiated by an ET, a radical and/or an anion intermediate somewhere along the reaction path may isomerize, so in this case the product distribution will mirror the thermodynamic stability of the two isomers. This expectation is born out in practice.[2e,6] It is important to note, however, that several alternative *polar* pathways can result in net *syn*-elimination or isomerization.[4]
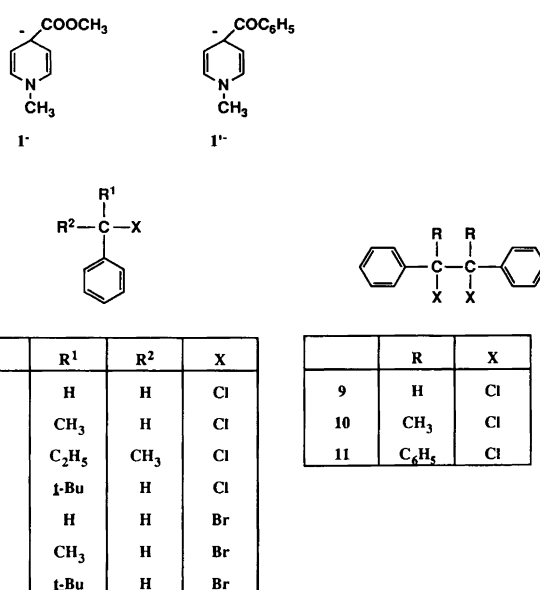
Kinetic measurements. The transition state of an S_N2 reaction is substantially stabilized by the bond formation, for example the stabilization in the reaction between iodide and ethyl bromide is estimated to be approximately 29 kcal mol^{-1}.[2b] This stabilization lowers the barrier of the reaction and hence makes the reaction proceed faster than the corresponding outer-sphere ET. By comparing the rate constant (k_{SUB}) of the nucleophilic substitution reaction between a nucleophile Nu and a substrate RX with the rate constant (k_{ET}) of the reaction between an outer-sphere electron donor with the same standard potential E°_{Nu} and self-exchange reorganization energy as the nucleophile and RX, one gets a measure of the rate enhancement in the nucleophilic substitution reaction. If the ratio k_{SUB}/k_{ET} is ca. 1 it can be concluded that there is no stabilization of TS, and consequently the

rate-determining step is the transfer of an electron from Nu to RX. If, however, $k_{SUB}/k_{ET} \gg 1$ there is some stabilization of TS due to bond formation, indicating that the nucleophilic reaction has a certain degree of S_N2 or inner-sphere ET character. In this kind of measurement entropy effects are assumed to be small.

In Red-E2 reactions the TS is characterized by a degree of bond formation between the nucleophile and the atom X and developing π-character of the bond between the two carbon atoms. This results in a more stabilized TS than for the outer-sphere ET, in which there is no bond formation. Consequently, by measuring the ratio k_{ELIM}/k_{ET}, where k_{ELIM} denotes the rate constant of the elimination reaction, and k_{ET} has the same meaning as above, one gets the same sort of information about an elimination reaction as measurements of k_{SUB}/k_{ET} give about a nucleophilic substitution reaction.

This kind of investigation has been applied to reactions between various nucleophiles, in particular the anions of 4-methoxycarbonyl-1-methyl-1,4-dihydro-pyridine (1$^-$) and 4-benzoyl-1-methyl-1,4-dihydro-pyridine (1$'^-$) (Scheme 2) and the superoxide ion $O_2^{-\cdot}$, and a number of alkyl halides and vicinal dichlorides.[2] So far it has been possible to find k_{SUB}/k_{ET} values ranging from one to 10^{12} corresponding to a stabilization of the TS of between 0 and 17 kcal mol^{-1}.

Measurements of activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. The loss of entropy on going from the reactant state to the transition state is larger in the polar than in the ET pathway owing to the association in the transition state and the restrictions on the transition-state geometry in an S_N2 or E2 reaction as compared with an outer-sphere ET. A polar reaction is therefore expected to show a lower

	R^1	R^2	X
2	H	H	Cl
3	CH$_3$	H	Cl
4	C$_2$H$_5$	CH$_3$	Cl
5	*t*-Bu	H	Cl
6	H	H	Br
7	CH$_3$	H	Br
8	*t*-Bu	H	Br

	R	X
9	H	Cl
10	CH$_3$	Cl
11	C$_6$H$_5$	Cl

Scheme 2.

(i.e., more negative) entropy of activation ($\Delta S^{\ddagger}$) than its ET counterpart. As a consequence of the bond formation in the TS of a polar reaction, the activation enthalpy ($\Delta H^{\ddagger}$) is expected to be smaller (i.e., less positive) than the $\Delta H^{\ddagger}$ of the corresponding ET reaction. By comparing the activation parameters of the nucleophilic substitution or the elimination with the values obtained for outer-sphere ET reactions, it should thus be possible to extract information about the mechanism of the former reactions. In the present investigation aromatic and heteroaromatic anion radicals were chosen as model outer-sphere electron donors. Nucleophilic substitution reactions between 1^- and a number of alkyl bromides have been studied in this manner, and indeed the variation of the activation entropy correlated well with the ET/S_N2 character estimated from k_{SUB}/k_{ET} measurements.[3b]

The aim of the present work was to cast further light on some reactions on the borderline between a polar and a non-polar mechanism by applying this kind of investigation to nucleophilic substitutions of 1^- with substituted benzyl chlorides such as benzyl chloride (2), 1-chloro-ethylbenzene (3), 2-chloro-2-phenylbutane (4), 1-chloro-2,2-dimethylpropylbenzene (5), benzyl bromide (6), 1-bromoethylbenzene (7) and 1-bromo-2,2-dimethyl-propylbenzene (8) and reductive dehalogenation reactions between 1^- or $1'^-$ and derivatives of 1,2-dichloro-1,2-diphenylethane such as ($\pm$)- and meso-1,2-dichloro-1,2-diphenylethane, [($\pm$)- and meso-9], meso-2,3-dichloro-2,3-diphenylbutane (meso-10) and 1,2-dichloro-1,1,2,2-tetraphenylethane (11) (Scheme 2). The electron donors used in the corresponding outer-sphere ET reactions are anion radicals of aromatic or heteroaromatic compounds, where the unpaired electron is delocalized over a large π-electron system, and bis(diphenyl)-chromium(0).

Results and discussion

According to the Arrhenius equation $k_1 = A \exp(-E_A/RT)$, where k_1 denotes the rate constant for the reaction under investigation, a plot of $\ln k_1$ vs. T^{-1} should be a straight line, and from the slope the activation energy E_A may be obtained. With the knowledge of k_1 and E_A the activation enthalpy and activation entropy may be calculated from eqns. (1) and (2)[7] where E_A is in cal mol^{-1}; k and h are Boltzmann's and Planck's constants, respectively.

$$\Delta H_T^{\ddagger} = E_A - RT \qquad (1)$$

$$\Delta S_T^{\ddagger} = 2.303 \, R[\log k_1 - \log(ek/h) - \log T] + E_A T^{-1}$$

$$= 4.576(\log k_1 - 10.753 - \log T) + E_A T^{-1} \qquad (2)$$

The reaction scheme for the reaction of aromatic anion radicals with alkyl halides RX or vicinal dihalides RXY in aprotic solvents is well established[2] and the rate constants of electron transfer k_{ET} can be found by conventional electrochemical techniques or pulse radiolysis. The mechanisms of the substitution and elimination reactions

Table 1. Rate constants k_{ET} for the reaction between phenazine anion radical and 1,2-dichloro-1,1,2,2-tetra-phenylethane measured by cyclic voltammetry (CV)[30] or a potentiostatic method[31] at different temperatures.

T/K	$k_{ET}/M^{-1} s^{-1}$
327.1	2750[a]
310.9	970[a]
305.2	660[a]
299.1	405[a]
295.5	305[a]
292.1	225[a]
282.8	110[a]
279.8	82[a]
271.4	40[a]
264.3	20.4[a]
253.2	7.00[a]
251.2	4.70[b]
239.2	1.20[b]
223.7	0.30[b]

[a] Measured by CV. [b] Measured by a potentiostatic method.

with 1^- and $1'^-$ follow Scheme 1. When ET is the rate-determining step, there may, in principle, be competition between coupling and reduction in the reaction of Nu$^-$ with the alkyl radicals. This competition will depend upon the difference in standard potentials of the radicals involved.[8] The reduction process is favoured when the potential of Nu$^+$/Nu$^-$ is more negative than that of R$^-$/R$^-$, which is the case in the elimination reactions, whereas the preference of coupling, as found in all the substitution reactions, requires the reverse order of the potentials. Loss of a chlorine atom from the initially formed radical in the elimination reaction seems less likely.

In Table 1 are given all kinetic data for the reaction between phenazine anion radical and 1,2-dichloro-1,1,2,2-tetraphenylethane measured by two electrochemical techniques, and in Fig. 1 the corresponding plot of $\ln k_{ET}$ vs. $1000 \times T^{-1}$ is shown. The points are best represented by a single straight line as is the case in the 98
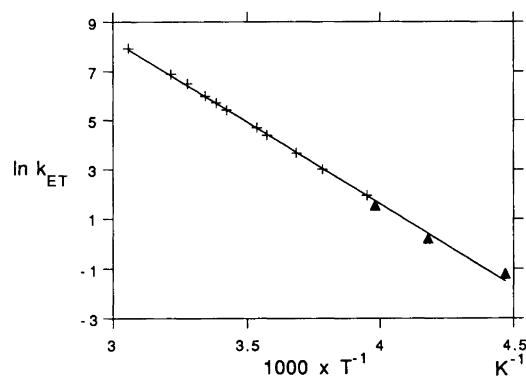

Fig. 1. Temperature dependence of the rate constant of the reaction between phenanzine anion radical and 1,2-dichloro-1,1,2,2-tetraphenylethane in DMF/TBABF$_4$, obtained by cyclic voltammetry (+) or homogeneous kinetic measurements using a rotating disk electrode (▲).

Table 2. Activation enthalpies $\Delta H^{\ddagger}_{298}$ in kcal mol^{-1} and activation entropies $\Delta S^{\ddagger}_{298}$ in cal mol^{-1} K^{-1} for reactions between a number of electron donors and electrophiles.

RX	A	$-E^{\circ}_A/V^a$	$\Delta H^{\ddagger}_{298}$	$\Delta S^{\ddagger}_{298}$
Benzyl chloride	Pyrene	1.618	5.7	−14.6
	Anthracene	1.490	5.9	−17.3
	9,10-Diphenylanthracene	1.394	7.4	−14.5
	Benzophenone	1.307	8.1	−15.8
	Perylene	1.213	9.1	−15.2
	Azobenzene[b]	0.879	11.2	−18.5
	1[−]	1.130	4.8	−23.5
1-Chloroethylbenzene	Pyrene	1.618	5.1	−17.1
	Anthracene	1.490	6.3	−15.7
	9,10-Diphenylanthracene	1.394	5.9	−18.4
	Benzophenone	1.307	8.8	−14.2
	Perylene	1.213	9.4	−14.3
	1[−]	1.130	6.0	−22.8
2-Chloro-2-phenylbutane	Pyrene	1.618	5.8	−16.8
	Anthracene	1.490	6.9	−15.4
	9,10-Diphenylanthracene	1.394	7.4	−15.9
	Benzophenone	1.307	10.2	−11.9
	Perylene	1.213	9.5	−14.3
	Azobenzene[b]	0.879	13.3	−14.8
	1[−b]	1.130	10.5	−16.8
1-Chloro-2,2-dimethylpropylbenzene	Quinoline	1.675	9.0	−11.5
	Pyrene	1.618	9.8	−10.8
	Anthracene	1.490	11.1	−10.8
	9,10-Diphenylanthracene	1.394	10.9	−12.9
	Benzophenone[b]	1.307	14.1	−8.3
	1[−b]	1.130	14.4	−13.0
Benzyl bromide	p-Diacetylbenzene	1.007	6.7	−18.5
	Azobenzene	0.879	8.6	−14.3
	p-Nitroanisole	0.784	9.3	−15.9
	Phenazine[b]	0.690	10.7	−14.3
	1-Nitronaphthalene[b]	0.600	12.1	−12.9
	Bis(diphenyl)chromium perchlorate[b]	0.300	16.3	−14.0
1-Bromoethylbenzene	p-Diacetylbenzene	1.007	6.1	−18.3
	Azobenzene	0.879	9.0	−12.8
	p-Nitroanisole	0.784	10.7	−11.6
	Phenazine[b]	0.690	10.2	−14.7
	1-Nitronaphthalene[b]	0.600	12.1	−13.1
	Bis(diphenyl)chromium perchlorate[b]	0.300	15.2	−13.4
1-Bromo-2,2-dimethylpropylbenzene	Benzophenone	1.307	9.6	−8.6
	Perylene	1.213	9.0	−10.6
	Tetracene	1.105	10.5	−10.6
	p-Diacetylbenzene	1.007	11.8	−9.4
	Azobenzene[b]	0.879	14.3	−7.1
	1[−]	1.130	10.9	−11.0
meso-1,2-Dichloro-1,2-diphenylethane	9,10-Diphenylanthracene	1.394	6.3	−13.3
	Benzophenone	1.307	9.4	−8.6
	Perylene	1.213	9.1	−9.7
	Acenaphthylene	1.190	9.2	−11.9
	Quinoxaline	1.189	10.0	−8.7
	1[−]	1.130	9.9	−13.1
(±)-1,2-Dichloro-1,2-diphenylethane	9,10-Diphenylanthracene	1.394	7.3	−12.3
	4-Methoxybenzophenone	1.371	8.3	−12.0
	Benzophenone	1.307	9.9	−9.5
	9,10-Diacetoxyanthracene	1.243	9.3	−12.5
	Perylene	1.213	10.0	−10.1
	Acenaphthylene	1.190	10.2	−11.5
	1[−b]	1.130	11.7	−8.5
meso-2,3-Dichloro-2,3-diphenylbutane	9,10-Diphenylanthracene	1.394	7.7	−12.4
	4-Methoxybenzophenone	1.371	8.8	−11.9
	Benzophenone	1.307	10.4	−8.6
	9,10-Diacetoxyanthracene	1.243	9.3	−12.9
	Perylene	1.213	9.6	−11.3
	Quinoxaline	1.189	10.3	−10.0
	1[−b]	1.130	12.0	−9.1
1,2-Dichloro-1,1,2,2-tetraphenylethane	2-Methoxyazobenzene	0.899	9.3	−11.0
	Azobenzene	0.879	9.6	−10.3
	4-Chloroazobenzene	0.783	10.5	−9.9
	Phenazine[c]	0.690	12.6	−4.4
	1'[−]	0.886	6.5	−18.3

[a]Vs. Ag/AgI. [b]Measured by a potentiostatic method. [c]Measured by two independent electrochemical techniques.

other reactions we have studied in this report and previously.[3b] These results indicate that, in the temperature interval investigated ($-50°C$ to $50°C$), *there is no change in the mechanism of the reaction between electron donors such as aromatic anion radicals,* $1^-,1'^-$ *and electrophiles such as benzyl halides RX or vicinal dichlorides RXY.* This conclusion is also in accordance with that reported previously for the reactions with alkyl bromides.[3b]

The values of the activation enthalpy $\Delta H^{\ddagger}_{298}$ and the activation entropy $\Delta S^{\ddagger}_{298}$ for all the reactions investigated are shown in Table 2. For a given substrate $\Delta H^{\ddagger}_{298}$ decreases as a function of the electron-donating abilities of the anion radicals ($-E^{\circ}_{A}$), while the $\Delta S^{\ddagger}_{298}$ values including the one of bis(diphenyl)chromium(0) are reasonably constant. On the assumption that the solvation entropies $\Delta S^{\ddagger}_{sol}$ of the different donors do not differ appreciably, a possible interpretation of the latter trend is that the transition states within the whole series of electron donors investigated experience approximately the same steric congestion. Even though the solvation of bis(diphenyl)chromium(0) is expected to be different from the corresponding solvation of an anion radical owing to the different charges, the measurements of small entropies (-1 to -5 cal K^{-1} mol^{-1}) for the reduction of a number of aromatic compounds to the corresponding anion radicals in N,N-dimethylformamide (DMF)[9] have shown that this effect on $\Delta S^{\ddagger}_{298}$ should be small.

In Table 3 the values of $\Delta S^{\ddagger}_{298,A}$ and $\Delta S^{\ddagger}_{298,Nu}$ for the reactions between the aromatic anion radicals/$1^-/1'^-$ and the substrates RX and RXY are given. The values of $\Delta S^{\ddagger}_{298,A}$ for a given RX and RXY are obtained as the average of the relatively constant $\Delta S^{\ddagger}_{298}$ values given in Table 2. A direct comparison of the individual $\Delta S^{\ddagger}_{298,A}$ values is only possible if the contribution from $\Delta S^{\ddagger}_{sol}$ of the different RX and RXY are assumed to be constant. As long as the leaving group X is the same this is a reasonable approximation, but it seems more questionable when the leaving group is changed from bromide to chloride. In the TS the R–X bond is stretched to the point of breaking and an appreciable amount of the negative charge is localised on X. The difference in standard solvation entropies of

Cl^- and Br^- in DMF has been estimated to be near 6.5 cal K^{-1} mol^{-1} at 298 K.[10] However, since the R–X bond in the reactant state is more polarized in the chloro than in the bromo substrate, the difference in $\Delta S^{\ddagger}_{sol}$ between the two halide groups is, all things considered, expected to be less than 6.5 cal K^{-1} mol^{-1} and probably in the order of 2–3 cal K^{-1} mol^{-1} with the chloro substrates having the more negative value. For the sterically hindered substrates this seems to be a reasonable estimate.

The absolute values of $\Delta S^{\ddagger}_{298,A}$ for the compounds investigated are rather similar, but show a small consistent and interesting trend. The sterically less hindered halides benzyl chloride, 1-chloroethylbenzene, benzyl bromide and 1-bromoethylbenzene have a more negative value than the sterically more hindered halides such as 1-bromo-2,2-dimethylpropylbenzene, 1-chloro-2,2-dimethylpropylbenzene, ($\pm$) and *meso*-1,2-dichloro-1,2-diphenylethane, *meso*-2,3-dichloro-2,3-diphenylbutane and 1,2-dichloro-1,1,2,2-tetraphenylethane. This characteristic was also found for the alkyl bromides previously investigated. A likely interpretation is that the transition state in the former cases requires more defined stereochemistry than the sterically more hindered alkyl halides, and that this is an indication of a weak bonding between the electron donor and the substrate in the transition state. If so the reaction between aromatic anion radicals and these halides seems not to be a pure outer-sphere electron transfer, but has some inner-sphere ET character. 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. Surprisingly the $\Delta S^{\ddagger}_{298,A}$ value for the rather sterically hindered 2-chloro-2-phenylbutane is close to that for benzyl chloride and 1-chloroethylbenzene. This result indicates that $\Delta S^{\ddagger}$ may be influenced by things other than those proposed.

The determination of the activation entropies $\Delta S^{\ddagger}_{298,Nu}$ for the substitution reactions with the enolate ion 1^- was not possible in all cases (benzyl bromide, 1-bromoethylbenzene and 1,2-dichloro-1,1,2,2-tetraphenylethane) owing to the reactions being too fast ($k_{SUB}, k_{ELIM} >$

Table 3. Some activation parameters for the reactions between aromatic anion radicals or the nucleophile 1^- with alkyl halides. $\Delta S^{\ddagger}$ in cal mol^{-1} K^{-1} and $\Delta\Delta G^{\ddagger}_{298,\Delta S} = 298 \times (\Delta S^{\ddagger}_{298,ET} - \Delta S^{\ddagger}_{298,Nu})$ in kcal mol^{-1}.

Alkyl halide	$\Delta S^{\ddagger}_{298,A}$	$\Delta S^{\ddagger}_{298,Nu}$	$\Delta\Delta G^{\ddagger}_{298,\Delta S}$
Benzyl bromide	-15.0	—	—
1-Bromoethylbenzene	-14.0	—	—
1-Bromo-2,2-dimethylpropylbenzene	-9.3	-11.0	0.5
Benzyl chloride	-16.0	-23.5	3.8
1-Chloroethylbenzene	-15.9	-22.8	3.5
2-Chloro-2-phenylbutane	-14.8	-16.8	1.8
1-Chloro-2,2-dimethylpropylbenzene	-10.9	-13.0	0.6
meso-1,2-Dichloro-1,2-diphenylethane	-10.4	-13.1	0.7
($\pm$)-1,2-Dichloro-1,2-diphenylethane	-11.3	-8.5	-0.7
meso-2,3-Dichloro-2,3-diphenylbutane	-11.4	-9.1	-0.5
1,2-Dichloro-1,1,2,2-tetraphenylethane	-10.4	-18.3^a	2.2^a

^{a}Values given for the reaction with $1'^-$.

10^5 M^{-1} s^{-1} at 298 K) for precise measurements. However, for the reaction between 1,2-dichloro-1,1,2,2-tetraphenylethane and $1'^-$, $\Delta S^{\ddagger}_{298,Nu}$ was measurable. The reactivity of $1'^-$ has previously[2b] been shown to resemble that of 1^-, except that nucleophilic substitution reactions with $1'^-$ exhibit somewhat more inner-sphere character than the corresponding reactions with 1^-. The solvation entropies of the anions 1^- and $1'^-$ are most likely very similar and close to those of the delocalized aromatic anion radicals, so it should be possible to compare all the results obtained with the different electron donors and nucleophiles directly. For the reactions investigated the $\Delta S^{\ddagger}_{298,Nu}$ values follow the same trend as $\Delta S^{\ddagger}_{298,A}$, only to a larger extent. The most sterically hindered alkyl halides have the same values of $\Delta S^{\ddagger}_{298,Nu}$ as the anion radicals, whereas benzyl chloride, 1-chloroethylbenzene and 1,2-dichloro-1,1,2,2-tetraphenylethane have values 6–8 cal mol^{-1} K^{-1} more negative. These results indicate an earlier change of mechanism in the reactions of 1^- and $1'^-$ compared with those of the anion radicals.

In order to describe the character of ET in the reactions with 1^- and $1'^-$ the comparison of $\Delta S^{\ddagger}_{298,Nu}$ with the expected outer-sphere ET values, $\Delta S^{\ddagger}_{298,ET}$, instead of the corresponding $\Delta S^{\ddagger}_{298,A}$ values are more illuminating. For this purpose the average value of $\Delta S^{\ddagger}_{298,A}$ (-10.9 cal mol^{-1} K^{-1}) measured for the sterically hindered chloro compounds is used as a standard measure of $\Delta S^{\ddagger}_{298,ET}$ for all the chloro compounds investigated. For the bromo compounds the value -9.3 cal mol^{-1} K^{-1} found for 1-bromo-2,2-dimethylpropylbenzene is used. In the fourth column of Table 3 the differences between the values expected for an outer-sphere ET and the ones measured with 1^- and $1'^-$ are translated into differences in activation energy due to the entropy effect, $\Delta \Delta G^{\ddagger}_{298,\Delta S}$, by the expression $\Delta \Delta G^{\ddagger}_{298,\Delta S} = 298 \times (\Delta S^{\ddagger}_{298,ET} - \Delta S^{\ddagger}_{298,Nu})$. A small value of $\Delta \Delta G^{\ddagger}_{298,\Delta S}$, as found for the sterically very hindered substrates, indicates that the rate-determining step in the substitution and elimination reactions is the transfer of an electron. 1,2-Dichloro-1,1,2,2-tetraphenylethane, 2-chloro-2-phenylbutane and especially the less sterically hindered benzyl halides show a higher $\Delta \Delta G^{\ddagger}_{298,\Delta S}$ values, which may be interpreted in terms of a slightly more polar TS. The steric hindrance in 1,2-dichloro-1,1,2,2-tetraphenylethane is probably close to that of *meso*-2,3-dichloro-2,3-diphenylbutane and certainly larger than in ($\pm$) and *meso*-1,2-dichloro-1,2-diphenylethane. The results thus show that in reductive dehalogenations with comparable degrees of steric hindrance $1'^-$ has a larger inner-sphere component than does 1^-, similar to that found for nucleophilic substitutions,[2b] even though 11 is a much better electron acceptor than 9 or 10.

The parameter $\Delta \Delta G^{\ddagger}_{298,\Delta S}$ is a tool for describing the structure of the TS in the substitution or the elimination reaction compared with an equivalent outer-sphere ET, but it does not give any direct measure of the magnitudes of the activation barriers involved as do the activation enthalpies. The activation enthalpy $\Delta H^{\ddagger}_{298,A*}$ for the reaction between an electron donor with the same standard

potential as the nucleophile and the substrate may be obtained by using eqn. (3).

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}. \tag{3}$$

Experimentally, plots of $\Delta G^{\ddagger}_{298,A}$ for dissociative ET to alkyl halides vs. the standard potential of anion radicals (E°_A) have been shown to follow a linear free energy relationship,[3b] so by extrapolating or interpolating the experimental values for $\Delta G^{\ddagger}_{298,A}$ to the standard potential of 1^- or $1'^-$ by linear least-squares analysis and using the average values of $\Delta S^{\ddagger}_{298,A}$ from Table 3, $\Delta H^{\ddagger}_{298,A*}$ can be found. That straight lines are found is, in general, also confirmed in the present work; however, in most of the plots of $\Delta G^{\ddagger}_{298,A}$ vs. E°_A the point corresponding to benzophenone anion radical was found to be somewhat above the line defined by the other anion radicals (Fig. 2). A recent investigation[11] shows that the self-exchange reorganization energy of benzophenone anion radical is about 3 kcal mol^{-1} higher than the (approximately constant) $\lambda(0)$ values of other aromatic anion radicals. The origin of this phenomenon is possibly that the charge is more localized in the benzophenone anion radical than in anion radicals of aromatic hydrocarbons. Even though the dependence of the activation energy on the driving force has not been established conclusively for dissociative ET,[3b,12] the influence of $\lambda(0)$ on the activation energy can be estimated by $\lambda(0)/8$ as predicted by Marcus theory[13] and Marcus' cross-relation.[14] Provided that $\Delta S^{\ddagger}_{298,A}$ is independent of the exact nature of the anion radical, this leads to an activation enthalpy approximately 0.4 kcal mol^{-1} higher for benzophenone than expected from the straight line of the $\Delta G^{\ddagger}_{298,A}$ vs. E°_A plot defined by the other anion radicals investigated. Within experimental error, this is what is found (Fig. 2). The effect of the higher $\lambda(0)$ value is, however, not larger than the experimental uncertainty on $\Delta G^{\ddagger}_{298,A}$ so we find it reasonable to include the points corresponding to benzophenone in the plots of $\Delta G^{\ddagger}_{298,A}$ vs. E°_A used to evaluate $\Delta H^{\ddagger}_{298,A*}$.
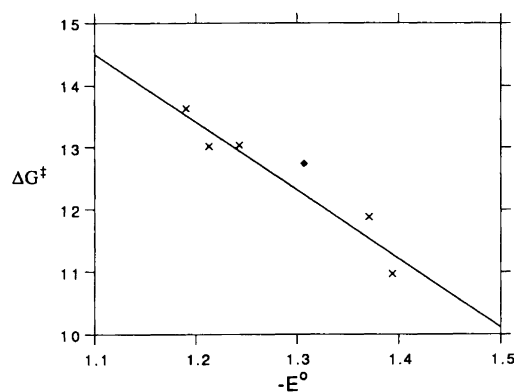

Fig. 2. A plot of $\Delta G^{\ddagger}_{298,A}$ vs. the standard potentials of different anion radicals $-E^{\circ}_A$ for the reaction with ($\pm$)-1,2-dichloro-1,2-diphenylethane ($\times$) including the one of benzophenone ($\blacklozenge$).

Table 4. Differences in activation enthalpy $(\Delta\Delta H^{\ddagger}_{298,A\bullet,Nu})$ between the reactions of alkyl halides with an anion radical with $E^{\circ}_{A} = E^{\circ}_{Nu}$ $(\Delta H^{\ddagger}_{298,A\bullet})$ and 1^{-} or $1'^{-}$ $(\Delta H^{\ddagger}_{298,Nu})$. $\Delta H^{\ddagger}$ in kcal mol^{-1}. The parameter k_{SUB}/k_{ET} is the ratio between the rate constants of the substitution reaction with Nu and the ET reaction with an anion radical with $E^{\circ}_{A} = E^{\circ}_{Nu}$.

Alkyl halide	$\Delta H^{\ddagger}_{298,A\bullet}$	$\Delta H^{\ddagger}_{298,Nu}$	$\Delta\Delta H^{\ddagger}_{298,A\bullet,Nu}$	k_{SUB}/k_{ET}
Benzyl bromide	6.3	—	—	—
1-Bromoethylbenzene	6.0	—	—	—
1-Bromo-2,2-dimethylpropylbenzene	10.8	10.9	−0.1	0.4
Benzyl chloride	9.6	4.8	4.8	83
1-Chloroethylbenzene	9.5	6.0	3.5	10
2-Chloro-2-phenylbutane	10.6	10.5	0.1	2.3
1-Chloro-2,2-dimethylpropylbenzene	14.8	14.4	0.4	0.8
meso-1,2-Dichloro-1,2-diphenylethane	10.1	9.9	0.2	0.54[a,b]
(±)-1,2-Dichloro-1,2-diphenylethane	10.8	11.7	−0.9	0.55[a,b]
meso-2,3-Dichloro-2,3-diphenylbutane	10.4	12.0	−1.6	0.2[b]
1,2-Dichloro-1,1,2,2-tetraphenylethane	9.6	6.5[c]	3.1[c]	3.9[b,c]

[a] From Ref. 2(e). [b] For the reductive eliminations the value k_{ELIM}/k_{ET} is given, where k_{ELIM} denotes the rate constant for the reaction between 1^{-} and the appropriate substrate. [c] Values given for the reaction with $1'^{-}$.

The thus calculated $\Delta H^{\ddagger}_{298,A\bullet}$ values are listed in Table 4 together with $\Delta H^{\ddagger}_{298,Nu}$ and the difference $\Delta\Delta H^{\ddagger}_{298,A\bullet,Nu} = \Delta H^{\ddagger}_{298,A\bullet} - \Delta H^{\ddagger}_{298,Nu}$. Values of k_{SUB}/k_{ET} and k_{ELIM}/k_{ET} are listed in column 5. The development in $\Delta\Delta H^{\ddagger}_{298,A\bullet,Nu}$ and k_{SUB}/k_{ET} or k_{ELIM}/k_{ET} follows that of $\Delta\Delta G^{\ddagger}_{298,\Delta S}$ with the smallest values found for the sterically most hindered substrates. For the substitution reactions investigated with 1^{-}, the development in all three kinds of parameter is thus interpreted to suggest a gradual change in the reaction mechanism from a pure outer-sphere dissociative ET followed by a radical coupling for a sterically hindered substrate to a mechanism involving some bonding stabilization of the TS when the steric hindrance diminishes. According to the measurements of entropy the $\Delta\Delta H^{\ddagger}_{298,A\bullet,Nu}$ and k_{SUB}/k_{ET} (k_{ELIM}/k_{ET}) parameters do not give a totally correct measure of the ET character in the substitution reactions of the less sterically hindered substrates such as benzyl chloride, 1-chloroethylbenzene and 2-chloro-2-phenylbutane, since the possible inner-sphere character in the standard reaction with the anion radicals has not been taken into account. For instance the $\Delta\Delta H^{\ddagger}_{298,A\bullet,Nu}$ value predicts the reaction of 2-chloro-2-phenylbutane to be an outer-sphere ET, while the corresponding $\Delta\Delta G^{\ddagger}_{298,\Delta S}$ predicts less ET character.

Other workers have previously determined activation parameters for some reductive dehalogenation and substitution reactions in DMF. Some results collected from various sources in the literature are presented in Table 5. The only results directly comparable to ours are the $\Delta S^{\ddagger}_{298}$ values from the reaction between perylene anion radical and r-1,t-2-dibromo-c-4-methylcyclohexane (entry 8) and the reaction between anthracene anion radical and $tert$-butyl bromide (entry 10). In both cases they are close to the value we found for an outer-sphere ET mechanism.

Stereochemical results of the reductive dehalogenation of (±)-1,2-dibromo-1,2-diphenylethane by SnCl$_2$ suggest that SnCl$_2$ acts as an outer-sphere electron donor, since the product is almost entirely (E)-stilbene.[15] A very similar outcome is observed in the reaction with Br^{-}, for

which an ET mechanism seems unlikely. In the latter case, a stepwise mechanism, the formation of a bridged species which may isomerize, presumably via an open carbonium ion, has been suggested.[4] A competing S_N2-E2 route has also been invoked to explain this result.[4] Such suggestions might also be considered for the SnCl$_2$ induced reactions. When compared with the results of our work the activation entropies found for the reactions between SnCl$_2$ and (±)- and meso-1,2-dibromo-1,2-diphenylethane (entries 6 and 7) are clearly much more negative than expected for an outer-sphere ET. This seems to indicate that there is some bonding in the TS of these reactions. Another possible explanation is, however, that SnCl$_2$ is uncharged. Consequently the reactant state has no charge separation in contrast with the TS, where the solvent molecules are therefore more strictly oriented. This would lead to a more negative activation entropy.

The measurements of activation parameters for reductive debrominations of (±)- and meso-1,2-dibromo-1,2-diphenylethane by halide ions show some interesting trends (entries 1 to 5). The $\Delta H^{\ddagger}_{298}$ of the reactions with the (±)-isomer is 6–8 kcal mol^{-1} higher than the $\Delta H^{\ddagger}_{298}$ of the corresponding reactions with the meso-isomer. The same trend is found in our results for the reactions with (±)- and meso-1,2-dichloro-1,2-diphenylethane, but to a much smaller extent (Table 4). The reason for the large difference in $\Delta H^{\ddagger}_{298}$ in the reactions with halide ions as compared with our results is probably the polar character of the transition state. In the TS of a polar reaction, the C=C double bond formation has progressed to a large extent, so the two phenyl groups are close to being in the same plane. In the (±)-isomer the phenyl groups are on the same side of the developing C=C double bond, and consequently they will be in an almost eclipsed conformation. This destabilizes the TS of the (±)-isomer substantially compared with the TS of the meso-isomer.[16] In the ET reaction the halogen atoms must also be arranged in the antiperiplanar configuration,[17] but owing to the lack of double-bond formation, the phenyl groups of the

Table 5. Activation parameters previously published for reductive eliminations and nucleophilic substitutions in DMF. $\Delta H^{\ddagger}$ in kcal mol^{-1} and $\Delta S^{\ddagger}$ in cal mol^{-1} K^{-1}.

Entry	Nucleophile	Substrate	$\Delta H^{\ddagger}_{298}$	$\Delta S^{\ddagger}_{298}$	Ref.
1	Li$^+$Br$^-$	meso-1,2-Dibromo-1,2-diphenylethane	20.6	−8.8	19[a]
2	Li$^+$Br$^-$	(±)-1,2-Dibromo-1,2-diphenylethane	28.9	8.9	19[a]
3	Na$^+$I$^-$	meso-1,2-Dibromo-1,2-diphenylethane	16.3	−15.1	20
4	Na$^+$I$^-$	(±)-1,2-Dibromo-1,2-diphenylethane	22.3	−6.9	20
5	Li$^+$Cl$^-$	meso-1,2-Dibromo-1,2-diphenylethane	21.7	−8.8	15[a]
6	SnCl$_2$	meso-1,2-Dibromo-1,2-diphenylethane	15.5	−27.7	15[a]
7	SnCl$_2$	(±)-1,2-Dibromo-1,2-diphenylethane	19.3	−21.0	15[a]
8	Perylene anion radical	r-1, t-2-Dibromo-c-4-methylcyclohexane	7.4	−9.5	32[b]
9	OEPFe(I)	r-1, t-2-Dibromo-c-4-methylcyclohexane	8.5	−3.3	32[b]
10	Anthracene anion radical	tert-Butyl bromide	10.4	−8.0[c]	3(a)
11	OEPFe(I)	Butyl bromide	6.5	−28.0[c]	3(a)
12	ETIOPFe('0')	Butyl bromide	2.3	−27.0[c]	3(a)
13	ETIOPFe('0')	2-Butyl bromide	11.0	−2.0[c]	3(a)
14	ETIOPFe('0')	tert-Butyl bromide	10.0	−7.7[c]	3(a)
15	TPPFe('0')	Butyl bromide	3.4	−28.0[c]	3(a)

[a] In the references the activation parameters are calculated at 59.4°C, but in this table the values at 298 K are calculated from the kinetic data given in the reference for the sake of comparison. [b] The numbers are calculated from the Arrhenius plot published in the reference as kinetic data are not available. [c] Recalculated with the use of eqns. (1) and (2). OEPFe(I), ETIOPFe('0') and TPPFe('0') are abbreviations for octaethylporphyrinoiron(I), tetraethyltetramethylporphyrinoiron('0') and tetraphenyl-porphyrinoiron('0'), respectively.

(±)-isomer will only be in a gauche position, towards which the barrier is smaller than to the eclipsed configuration. Hence the difference in $\Delta H^{\ddagger}_{298}$ between the two isomers should be smaller in the ET reaction than in its polar counterpart. The difference in ΔG°_f for (Z)- and (E)-stilbene is 3.8 kcal mol^{-1} in DMF at 60°C,[18] and $(\Delta G^{\circ}_{f,\pm} - \Delta G^{\circ}_{f,meso})$ is 0.78 kcal mol^{-1},[15] so $(\Delta G^{\ddagger}_{\pm} - \Delta G^{\ddagger}_{meso})$ should not be more than 3 kcal mol^{-1}. Assuming that the entropy effects are small, this is also a rough estimate of the maximum difference in activation enthalpy for the polar eliminations, so the explanation above can only partly account for the dramatic difference between the results of Miller et al.[19,20] and our results.

The values of the activation entropies for the reactions of the halide ions in entries 1, 3, 4 and 5 are close to $\Delta S^{\ddagger}_{298,ET}$, and are even more positive for the reaction in entry 2, which seems quite surprising if the activation entropy is expected to reflect the degree of order in the transition states. With the polar nature of the reactions, the $\Delta S^{\ddagger}_{298}$ values would be expected to be more negative than $\Delta S^{\ddagger}_{298,ET}$ we have found for a pure outer-sphere ET reaction. It is, however, questionable how significant the direct comparison of activation entropies is. Firstly it is a rather crude approximation that the solvation entropies of the halide ions are close to those of the large aromatic anion radicals and anions we have used. The solvation entropies are much less negative for the anion radicals (probably in the order of 40 cal mol K^{-1}).[9,10,21] Secondly,

the experiments with halide ions were carried out with alkali-metal ions (Li$^+$ and Na$^+$) as counterions, and the extent of ion pairing is probably much larger in that case than with tetrabutylammonium as a counterion. For the sake of comparison it would be useful to measure the activation parameters with the tetrabutylammonium salts of the halides in order to eliminate the effect of ion pairing. In any case there is no obvious reason that the reactions between Br$^-$ and the two different isomers of 1,2-dibromo-1,2-diphenylethane should exhibit any significant difference in the contribution from the solvent to the activation entropy, so a priori the different activation entropies must reflect different degrees of order in the corresponding transition states, but it is not clear why the difference between the two isomers should be so dramatic as to cause the $\Delta S^{\ddagger}_{298}$ to be positive for the (±)- and negative for the meso-isomer. The experiments with (±)-1,2-dibromo-1,2-diphenylethane and Br$^-$ were carried out in the presence of SnCl$_2$, which itself reacts with the substrate.[19] It is claimed that the kinetics of the reaction with bromide can be distinguished from those of the reaction with stannous chloride. However, introducing SnCl$_2$ into the reaction makes it uncertain which is actually the reducing agent, and furthermore it is possible that the stannous chloride coordinates with the nucleophile and/or the substrate and thus changes the geometry of the TS. The possibility of competing reactions and/or coordination in the case of the studies on the

reaction between $(\pm)$-1,2-dibromo-1,2-diphenylethane and bromide ion, in our opinion, makes these results unsuitable for direct comparison with the results obtained in the present work.

For the delocalized iron porphyrin complexes it seems to be a more appropriate assumption that the solvation entropies are comparable to the corresponding entropies of the anion radicals/1^-/$1'^-$. Although the Fe('0') complexes have a double negative charge the effect on the solvation entropy will probably be rather small.[22] From the kinetic measurements of k_{SUB}/k_{ET} and k_{ELIM}/k_{ET} (estimated from the data given in the references) only the reaction in entry 14 ($k_{SUB}/k_{ET} \approx 3$) is expected to be an outer-sphere ET, while especially the reactions in entries 9, 11 and 15 (k_{SUB}/k_{ET}, $k_{ELIM}/k_{ET} \approx 10.000$) should show some inner-sphere ET character. The k_{SUB}/k_{ET} values estimated for the reactions in entries 12 and 13 are 300 and 15, respectively. Four of the values (entries 11, 12, 14 and 15) are in accordance with the expectations from the kinetic measurements and our results. On the other hand, the $\Delta S^{\ddagger}_{298}$ for the reactions of OEPFe(I) and r-1, t-2-dibromo-c-4-methylcyclohexane and of ETIOPFe('0') with 2-butyl bromide are more positive than for an outer-sphere ET, even though the kinetic data suggest these reactions to be of the inner-sphere ET type. At the moment it is difficult to give an explanation for these results.

Conclusions

Activation parameters for nucleophilic substitution reactions of various benzyl halides such as benzyl chloride, 1-chloroethylbenzene, 2-chloro-2-phenylbutane, 1-chloro-2,2-dimethylpropylbenzene, benzyl bromide, 1-bromoethylbenzene and 1-bromo-2,2-dimethylpropylbenzene and reductive dehalogenations of vicinal dichlorides such as $(\pm)$- and $meso$-1,2-dichloro-1,2-diphenylethane, $meso$-2,3-dichloro-2,3-diphenylbutane and 1,2-dichloro-1,1,2,2-tetraphenylethane have been measured in order to obtain information about the degree of outer-sphere or inner-sphere ET in the reactions. In the present case the reactions between the sterically hindered benzyl halides or the vicinal dihalides and the aromatic anion radicals all show the characteristics of an outer-sphere ET, i.e., a rather small negative activation entropy (about -10 cal mol^{-1} K^{-1}), while the reactions with the sterically less hindered alkyl halides have some inner-sphere character. Furthermore the plots of $\Delta G^{\ddagger}_{298,A}$ vs. $-E^{\circ}_A$ were all linear except for minor deviations that could be explained by a larger self-exchange reorganization energy for the corresponding anion radical (benzophenone). In agreement with previous work,[3b] it is found that in the reactions between 1^- and the substrates investigated, the change from a pure outer-sphere ET mechanism to a reaction with some inner-sphere character occurs earlier than for the anion radicals. The conclusions pertaining to the ET character of the reactions with 1^- derived from the present investigation are in good accord with those drawn

earlier on the basis of kinetic measurements, and it can thus be concluded that the present method supplements the kinetic investigations.

The experimental evidence presented in this paper does not enable one to decide conclusively whether the mechanism of a given reaction is a true competition between ET and the classical polar pathway, or should rather be viewed as a hybrid of the two. However, the Arrhenius plots for the different substitution and elimination reactions investigated in this work are all best represented by a $single$ $straight$ $line$. The reactions with the enolate anion 1^- studied in this and in earlier[3b] work cover a wide range of k_{SUB}/k_{ET} ratios, and one would thus expect that if there is a change in mechanism from S_N2 or E2 at low temperatures to ET at higher temperatures, the change should occur at $different$ temperatures in the reactions, we have studied. The fact that $none$ of the Arrhenius plots show a change of the slope in the temperature range encountered here, in our opinion, points to a continuous spectrum of reactions between a polar and an ET mechanism being a better model to describe nucleophilic substitutions and reductive eliminations than two distinct and competing pathways. The evidence in favour of either of the two viewpoints is, however, not conclusive.

Experimental

$Materials.$ $meso$- and $(\pm)$-1,2-Dichloro-1,2-diphenylethane,[23] $meso$-2,3-dichloro-2,3-diphenylbutane,[24] 1,2-dichloro-1,1,2,2-tehtraphenylethane,[25] 1-bromo-2,2-dimethylpropylbenzene[26] and bis(diphenyl)chromium perchlorate[27] were prepared according to the references given. The crude product of 1-bromo-2,2-dimethylpropylbenzene was purified by flash chromatography through a silica gel column with petrol ether as the eluent. 2-Chloro-2-phenylbutane was obtained from 2-phenyl-2-butanol, which was prepared in the Grignard reaction between acetophenone and C_2H_5MgBr, by treatment with hydrogen chloride in methylene chloride. 1-Chloroethylbenzene was prepared similarly from 1-phenylethanol.

Azobenzene, acenaphthylene and quinoxaline were recrystallized once or twice from ethanol prior·to use. 4-Chloroazobenzene and 2-methoxyazobenzene were prepared as in Refs. 28 and 29, respectively. All other mediators were used as received.

The supporting electrolyte (tetrabutylammonium tetrafluoroborate, $TBABF_4$) and the solvent (N,N-dimethylformamide, DMF) were purified using standard procedures. Before each experiment the electrolyte solution was dried by passage through a column of activated alumina.

$Instrumentation.$ The recording system and potentiostat have been describes previously.[30] The working electrode used (gold or platinum microelectrodes of diameter 0.3–0.6 mm) was polished before each experiment. The rotating disk electrode was a gold electrode of diameter 3 mm. The reference electrode was a silver wire in $TBABF_4$/DMF; potentials were checked afterwards against the redox potential of anthraquinone.

Procedure. Measurement of the rate constants by cyclic voltammetry (CV) were performed by the method described by Pedersen and Svensmark.[30] The cell was immersed in a Dewar flask containing water (0–50°C), acetone or ethanol ($<0°C$). The temperature of the cell was measured with a NiCrAl temperature probe, which was put inside a glass tube containing acetone. The temperature probe was connected to a Lutron TM-905 digital thermometer. Values of rate constants less than $10 \, M^{-1} \, s^{-1}$ were measured by means of a potentiostatic method using a rotating disk electrode following the procedure described in Ref. 31. In some of the experiments with 1^-, the anion was produced indirectly by first reducing an appropriate amount of anthracene preparatively to the anion radical and then adding a solution of $1^+ClO_4^-$ in carefully deaerated DMF. This procedure generated 1^- faster than the direct reduction of the perchlorate salt of 1^+ could do, especially at low temperatures.

Most of the CV experiments with 1^- were carried out in largely the same manner as for anion radicals, except that the electrode was held at a potential cathodic of the $1^+/1^{\bullet}$ wave between experiments thereby saturating the diffusion layer with $1^{\bullet}$. If this diffusion layer is stable during the time of the CV scan, only one electron will be transferred per molecule of the mediator. However at slow scan rates ($<500 \, mV^{-1}$) the diffusion layer may be distorted during the time of the scan and thus permit some 1^+ to reach the electrode. In this case the number of electrons transferred will be higher than one per molecule, and proper data treatment will be hampered. To avoid this difficulty some of the CV experiments with 1^- were carried out in the following way. The cathode chamber of a conventional H-cell was equipped with a platinum net, a gold microelectrode, a reference electrode and a glass tube with the temperature probe. Thirty ml of a solution of $1^+ClO_4^-$ (1–2 mM) was poured into the cathode chamber, and the other two chambers of the cell were filled with the appropriate amount of solvent with supporting electrolyte. The catholyte was carefully deaerated with N_2 or Ar, and a check was made to see whether the $1^{\bullet}/1^-$ wave was reversible in CV, using the microelectrode as the working electrode and the platinum net as counter electrode. A potentiostat for preparative purposes was then connected to the platinum net, and 1^+ was reduced preparatively to $1^{\bullet}$ at the net with a carbon electrode in the anodic chamber serving as the counter electrode. The reduction was stopped when a little less than $1 \, F \, mol^{-1}$ has passed in order not to generate any 1^-. After the preparative reduction the cathodic peak current in CV was measured at two or three different scan rates and compared with the peak current measured at the same scan rates before the electrolysis. If the current had dropped by more than 10%, the solution was discarded and a new one was prepared. A solution of the substrate in 2.0 ml of carefully deaerated solvent was added to the cell, and CV experiments could then be carried out in the manner described for anion radicals. The radical $1^{\bullet}$ is sensitive to molecular oxygen, so during these experi-

ments great care was taken to exclude dioxygen from the cathode chamber. However, with the working conditions described above, the solution of $1^{\bullet}$ was stable for 1–2 h, which sufficed to measure the rate constant at 8 to 10 different temperatures.

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