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Electron Transfer in Some Nucleophilic Reactions

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Abstract. Using kinetic, steric and thermodynamic results it is argued that the rate-determining step in some aliphatic, nucleophilic substitutions is the transfer of an electron.

Electron transfer in organic chemistry has been discussed for more than 30 years. The arguments used to substantiate the claim of the involvement of electron transfer have varied, and not all the arguments used in the discussion have been convincing. The distinction between an outer-sphere electron transfer reaction, an inner-sphere electron transfer reaction and a polar reaction is often difficult to make and even the use of these conceptions is not always clear.

In this communication we attempt to illustrate how electrochemical methods may be used in investigations of nucleophilic reactions with special emphasis on the aliphatic nucleophilic substitution.

Our work with indirect reduction of aryl and alkyl halides using aromatic radical anions as electron donors and the observed coupling between the alkyl radicals and the radical anions (Ref. 1) lead us to use electrogenerated anions as electron donors (Ref. 2). We first showed that electrogenerated anions could act as electron donors in an reductive elimination; the further observation that the electrogenerated anion of 4-methoxycarbonyl-1-methyl-1,4-dihydropyridine (**1**$^-$) reacted in DMF with *tert*-butyl bromide and *tert*-butyldimethylsulfonium iodide to 4-*tert*-butyl-4-methoxycarbonyl-1-methylpyridine (**3**) [eqn. (1)] (Ref. 2) lead us to a closer investigation of the aliphatic nucleophilic substitution. The reaction between **1**$^-$ and *tert*-butyldimethylsulfonium iodide (**2**) could not be a classical S_N2 reaction for steric reasons, the methyl groups in **2** would be attacked rather than the *tert*-butyl group; an S_N1 reaction is unlikely, as **2** did not form *tert*-butyl iodide in DMF in the presence of a large excess of tetrabutylammonium iodide. A reaction between the *tert*-butyl radical and **1**$^-$ in an $S_{RN}1$-like fashion is highly unlikely as the steady state concentration of the nucleophile **1**$^-$ is negligible under the reaction conditions.

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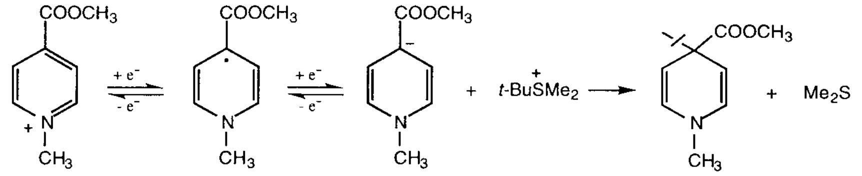


(1)

$\mathbf{1}^+$ $\mathbf{1}^{\cdot}$ $\mathbf{1}^-$ **2** **3**

It was therefore suggested that the enolate ion $\mathbf{1}^-$ had transferred an electron to the substrate which cleaved to a *tert*-butyl radical and the leaving group, and that the radical $\mathbf{1}\cdot$ and *tert*-butyl radical coupled to give the product. It was also proposed (Ref. 2) that there might be found reactions with transition states (TS) ranging from the classical S_N2 TS, with an approximately equal bonding of the cental carbon to both the incoming nucleophile and the leaving group, to an ET TS, in which there is a negligible bonding (the limit is usually arbitrarily put to 1 kcal mol $^{-1}$) between the nucleophile and the central carbon. In such a TS the distance between the nucleophile and the central carbon would be greater than in the classical S_N2 TS and the nucleophile would not need to attack along the C-X axis. The reaction between $\mathbf{1}^-$ and *tert*-butyl bromide could thus be described by eqn. (2).

$$\mathbf{1}^- + tert\text{-BuBr} \rightarrow [\ \mathbf{1}\cdot + tert\text{-Bu}\cdot + \mathrm{Br}^-\ ] \rightarrow \mathbf{3} + \mathrm{Br}^- \qquad (2)$$

To substantiate the suggestion that the reaction was, indeed, best described as an ET reaction we used the results from kinetic, steric and thermodynamic experiments (Refs. 3,4).

1. *Kinetic measurements.* The reactions between radical anions of aromatic and heteroaromatic compounds and alkyl halides have been described by the eqns. (3) to (6).

$$\mathrm{A} + e^- \rightleftarrows \mathrm{A}^{-\cdot} \qquad (3)$$

$$\mathrm{A}^{-\cdot} + \mathrm{RX} \xrightarrow{k_{ET}} \mathrm{A} + \mathrm{R}\cdot + \mathrm{X}^- \qquad (4)$$

$$\mathrm{A}^{-\cdot} + \mathrm{R}\cdot \xrightarrow{k_5} \mathrm{AR}^- \rightarrow \text{Products} \qquad (5)$$

$$\mathrm{A}^{-\cdot} + \mathrm{R}\cdot \xrightarrow{k_6} \mathrm{A} + \mathrm{R}^- \rightarrow \text{Products} \qquad (6)$$

The idea behind the kinetic test is to compare the rate constant k_{SUB} of the substitution of a nucleophile (*e.g.* $\mathbf{1}^-$) on a certain alkyl halide with the rate constant (k_{ET}) of an electron transfer to the same alkyl halide from an outer-sphere electron donor with the same standard potential and reorganization energy (λ) as the nucleophile. The ratio k_{SUB}/k_{ET} is a measure of the difference in the activation energy between the substitution reaction and the outer-sphere ET TS. If $k_{SUB}/k_{ET} \sim 1$ then the rate determining step would be assumed to be the transfer of an electron from the nucleophile to the alkyl halide for this aliphatic nucleophilic substitution (Ref. 5).

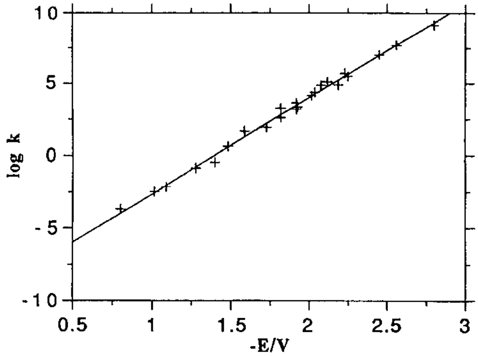
2. *Stereochemical probes.* A classical S_N2 reaction would result in an inversion of the configuration at the central carbon, whereas in a radical reaction a stereochemical equilibration would be expected, although it has been argued that an inversion does not exclude a radical reaction (Ref. 6). Under all circumstances a racemization would exclude an S_N2 mechanism.

3. *Activation parameters.* An S_N2 reaction would be expected to have, compared to an ET reaction, a relatively low enthalpy of activation due to the bonding stabilization in TS, and a relatively low ("more negative") entropy of activation. The S_N2 TS is tighter than the ET TS, and it is generally assumed that strict stereochemical requirements in the TS result in a lower $\Delta S^{\ddagger}$.

Kinetic test

For the kinetic test radical anions of aromatic hydrocarbons and heteroaromatic compounds were chosen as one-electron donors; such radical anions are stable in the absence of proton donors and they have a relatively low reorganization energy connected with the electron transfer. The reaction of an aromatic radical anion with an alkyl halide has mostly been assumed to be a dissociative electron transfer with no inner-sphere component; this is with a good approximation true for most secondary and tertiary alkyl bromides and iodides, but not for all alkyl chlorides; especially reactions between radical anions and methyl chloride have a very significant, potential-dependent S_N2 component in the mechanism (Ref. 7).

In Fig. 1 log k_{ET} of the reaction between aromatic radical anions and *tert*-butyl bromide is shown in dependence of the driving force; the fastest reactions ($k_{ET} > 10^7$ $M^{-1}s^{-1}$) have been measured by pulse radiolysis (Ref. 8).



In Fig. 1 a linear dependence is assumed, whereas the theory suggests a parabola (Ref. 9). Possibly an inner-sphere component becomes more significant for donors with higher redox potentials for which the ET becomes more endergonic and the reaction thus gradually develops more S_N2 character concurrently with the decrease of the rate of the ET. Together the range of rate constants spans 13 orders of magnitude, and as seen from Fig. 1 the points seem best represented by a straight line.

The reactions between nucleophiles and alkyl halides have been studied with similar methods as for the radical anions and the rate constant of the substitution reaction, k_{SUB}, measured. The logarithm of the ratio of the rate constants, k_{SUB}/k_{ET}, is a measure of the activation energy of the substitution reaction compared with that of the outer-sphere ET and is thus taken as an indication of the inner-sphere (S_N2) stabilization of the transition state.

In Fig. 2 the crosses represent rate constants for the ET reaction of aromatic anion radicals with isobornyl bromide (**4**), and the square the rate constant for the substitution reaction of $\mathbf{1}^-$ with **4**. As the k_{SUB} of $\mathbf{1}^-$ falls on the straight line through the points for k_{ET}, $k_{\mathrm{SUB}}/k_{\mathrm{ET}}$ ~1 in this case, and the rate-determining step for this aliphatic nucleophilic substitution is assumed to be the transfer of an electron.

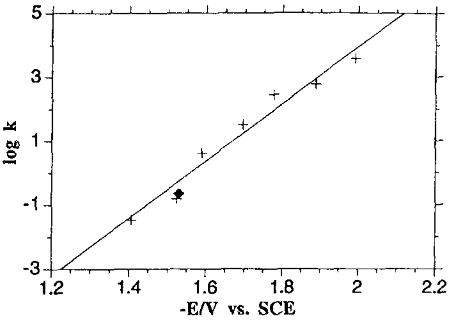


Fig. 2

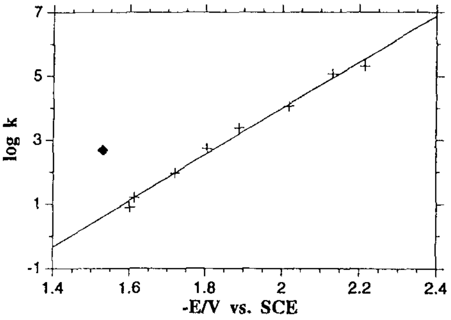


Fig. 3

In Fig. 3 similar data are presented for the reaction of $\mathbf{1}^-$ with 2-bromobutane (**5**). The ratio, $k_{\mathrm{SUB}}/k_{\mathrm{ET}}$, for **5** is 170 whereas it for ethyl bromide (**6**) is 2500. These numbers may indicate some bonding stabilization in the transition state compared to the outer-sphere ET reaction, or they may be interpreted as a result of a competition between two reaction paths, outer-sphere ET and classical S_N2. We prefer the former point of view, but there is no compelling experimental evidence either way.

If one accepts the model that the ET TS and the classical S_N2 TS with a significant bonding to both the incoming and leaving group leading to a stabilization (20 - 30 kcal mol^{-1}) in the TS are extremes and that there in between them exist transition states with different bonding stabilizations, then the reactions between $\mathbf{1}^-$ and **5** and **6** have transition states relatively close to the ET transition state as the bonding stabilization (2 - 5 kcal mol^{-1}) is relatively low. The situation with transition states between S_{ET} and the classical S_N2 is somewhat akin to that often suggested for the range of transition states in the S_N1-S_N2 reactions.

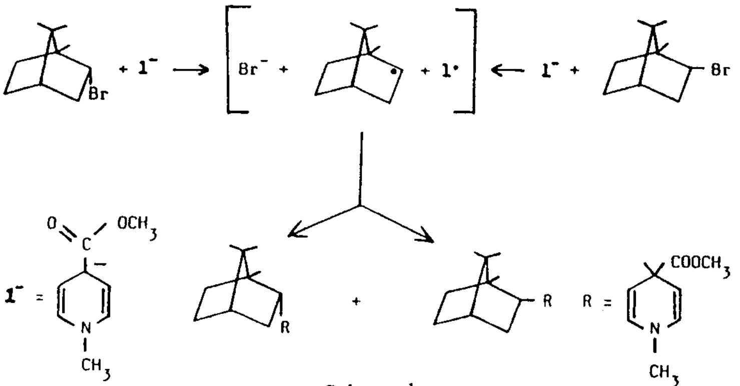
It would be of interest to use other nucleophiles than $\mathbf{1}^-$ (and similar anions with delocalized electron pair) in order to better bridge the gap between ET TS and a classical S_N2 TS. Superoxide, $O_2^{\cdot-}$, may react as a nucleophile and an electron donor. The directly measured values for $k_{\mathrm{SUB}}/k_{\mathrm{ET}}$ for the reaction between $O_2^{\cdot-}$ and some alkyl halides span a range from less than 0.6 for 1-iodoadamantane to $2\mathrm{x}10^9$ for butyl chloride; these $k_{\mathrm{SUB}}/k_{\mathrm{ET}}$ values may have to be multiplied by a factor ~ 500 due to the difference in the self-exchange reorganization energies between $O_2^{-\cdot}$ and the aromatic ET donors. Values of k_{SUB}/k_{ET} of 300 to 10^{12} correspond to stabilization energies ranging from below 4 kcal mol^{-1} to 17 kcal mol^{-1}. The results illustrate that the same nucleophile/electron donor may react mainly as an electron donor towards sterically very hindered alkyl halides and as a typical nucleophile with sterically less hindered electrophiles (Ref. 10).

Stereochemical investigations

A racemization in an aliphatic nucleophilic substitution would be expected only in the cases when $k_{SUB}/k_{ET} \sim 1$, and the synthetic difficulties of making an optically pure chiral tertiary halide and to establish the degree of chirality in the substitution products made us turn to the *exo/endo* relation of the bornyl system.

As is well-known the typical S_N2 reaction gives inversion at the central carbon atom. Reduction of anthracene in DMF in the presence of bornyl and isobornyl bromide (Ref. 11) gave the same 1:1 mixture of 9-(*exo*-2-bornyl)-9,10-dihydroanthracene and 9-(*endo*-2-bornyl)-9,10-dihydroanthracene; it happened to be an approximately 1:1 mixture of *exo* and *endo* product. When quinoxaline radical anion was used a predominant *endo*-substitution was found for both bornyl and isobornyl bromide.

The steric results indicate that in the reaction between anthracene radical anion and bornyl and isobornyl bromide the stereochemical information of the substrate is lost during the reaction; this is in accordance with the assumption that the reaction is an outer-sphere ET. This finding together with the evidence presented above further indicates that some aliphatic nucleophilic substitutions with aromatic radical anions may proceed through an outer-sphere ET and that the stabilization in the transition state is very small. In reactions with less sterically hindered alkyl halides an inner-sphere ET component may influence the stereochemical results (Ref. 7).



Scheme 1

Electrochemical reduction of 1^+ to 1^- in the presence of bornyl bromide (Scheme 1) in DMF gave two substitution products A and B in the proportion 1.4 : 1 (Ref. 12); when isobornyl bromide and 1^- reacted, the same substitution products A : B = 1 : 1.3 were found. The results are explicable if it is assumed that the 2-bornyl radical is a common intermediate in the reaction of 1^- with both bornyl and isobornyl bromide, Scheme 1. This suggests that when the kinetic results indicate $k_{SUB}/k_{ET} \sim 1$ then it may be expected that a predominant racemization takes place during the substitution. When $k_{SUB}/k_{ET} >> 1$ an inversion may be expected; in fact, the reaction between 1^- and optical active 2-bromobutane ($k_{SUB}/k_{ET} = 170$) gives more than 99 % inversion (Ref. 13).

Activation parameters

The entropy of activation for the S_N2 reaction should be lower ("more negative") than that of the ET reaction; this is, among other things, caused by the strict geometrical requirements and associative character of the S_N2-TS. On the other hand, the enthalpy of activation of the S_N2 reaction would be expected to be smaller than that of the ET reaction due to the bonding stabilization in the TS. In order to obtain these parameters the dependence of the rate of reaction on the temperature was measured. For a "well-behaved" reaction a linear connection between ln k and T^{-1} is expected from the Arrhenius equation.

All the reactions between different radical anions and alkyl bromides we have investigated showed a linear connection between ln k and T^{-1} (Ref. 14). This we interprete to show *that in the temperature interval investigated (-50 °C to 50 °C) there is no change detectable by this method in the mechanism of the reaction between aromatic radical anions and alkyl bromides* (Refs. 3,4).

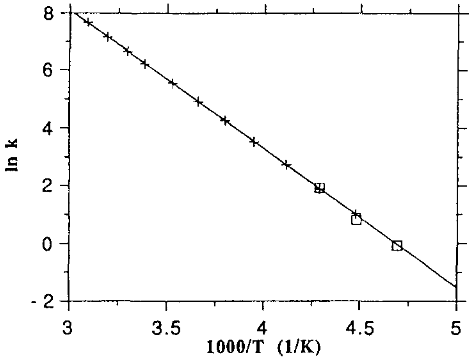


Fig. 4

From the Arrhenius plots the entropy and enthalpy of activation may be extracted (Ref. 14). In Table 1 are presented values of entropy of activation $\Delta S^{\ddagger}_{298}$ for the reaction between aromatic radical anions and some alkyl halides together with corresponding values for the reaction between $\mathbf{1}^{-}$ and the same alkyl halides.

In the reactions between radical anions and sterically hindered alkyl halides including *tert*-butyl bromide approximately the same value for $\Delta S^{\ddagger}_{298}$ is found, and this value is taken as standard value of $\Delta S^{\ddagger}_{298}$ for an outer-sphere dissociative ET. The somewhat lower values for $\Delta S^{\ddagger}_{298}$ for primary and secondary alkyl halides could be due to a bonding interaction in the TS, but other interpretations may be possible.

Table 1. Some activation parameters from the reactions between aromatic radical anions or $\mathbf{1}^{-}$ with alkyl halides. $\Delta S^{\ddagger}$ in cal mol^{-1}K^{-1} and $\Delta H^{\ddagger}$ and $\Delta\Delta G^{\ddagger}_{\Delta S} = 298(\Delta S^{\ddagger}_{298,A^{-\cdot}} - \Delta S^{\ddagger}_{298,\mathbf{1}^{-}})$ in kcal mol^{-1}.

	$\Delta S^{\ddagger}_{298,A^{-\cdot}}$	$\Delta S^{\ddagger}_{298,\mathbf{1}^{-}}$	$\Delta\Delta G^{\ddagger}_{\Delta S}$	$\Delta H^{\ddagger}_{298,A^{-\cdot}}$	$\Delta H^{\ddagger}_{298,\mathbf{1}^{-}}$	$\Delta\Delta H^{\ddagger}_{298,A^{-\cdot},\mathbf{1}}$	$\frac{k_{SUB}}{k_{ET}}$
Butyl	-16.4	-22.2	4.0	12.0	6.3	5.7	400
sec-Butyl	16.5	-21.2	3.7	11.6	7.4	4.2	170
tert-Butyl	-8.4	-15.8	2.2	13.4	11.1	2.3	2.5
exo-Norbornyl	-10.8	-16.2	1.6	15.4	13.2	2.2	1.7
1-Adamantyl	-7.6	-9.4	0.5	18.2	17.6	0.6	0.3
Bornyl	-8.7	-8.9	0.1	17.7	17.2	0.5	0.2

In the reaction with the enolate anion $\mathbf{1}^{-}$ only the most sterically hindered alkyl halides, 1-bromoadamantane and bornyl bromide, have the same values for $\Delta S^{\ddagger}_{298}$ as the aromatic radical anions. This is in accordance with the above-mentioned stereochemical results and the k_{SUB}/k_{ET} ~1 which indicates that for these sterically very hindered (against back-side S_N2 attack) alkyl halides the substitution reaction may be described as an outer-sphere dissociative ET followed by a radical coupling. The sterically less hindered alkyl halides, even *tert*-butyl bromide and *exo*-norbornyl bromide, show a lower ("more negative") $\Delta S^{\ddagger}_{298}$, which may be interpreted as a reaction with a slight inner-sphere stabilisation of the transition state. In the fourth column the difference between the values of the reaction with an outer-sphere electron donor ($\Delta S^{\ddagger}_{298,A^{-\cdot}}$ = -9 cal mol^{-1} K^{-1}) and with $\mathbf{1}^{-}$ is translated into differences in activation energy due to the entropy effect, $\Delta\Delta G^{\ddagger}_{\Delta S} = T(\Delta S^{\ddagger}_{298,A^{-\cdot}} - \Delta S^{\ddagger}_{298,\mathbf{1}^{-}})$.

In Table 1 also the values for the enthalpy of activation corresponding to the entropies are given in column 5 and 6 (Ref. 14). In the 7th column the difference $\Delta\Delta H^{\ddagger}_{298}$ between these values are given and in the last column the k_{SUB}/k_{ET} values are tabulated. As expected the primary and secondary alkyl halides have the highest values of $\Delta\Delta H^{\ddagger}_{298}$ indicating the higher stabilization of the TS in their reactions with $\mathbf{1}^{-}$. Again, only bornyl bromide and 1-bromoadamantane have the same enthalpy of activation in the reactions with $\mathbf{1}^{-}$ and with aromatic radical anions.

The results from the measurements of the activation parameters as well as those from the kinetic (k_{SUB}/k_{ET}) and stereochemical investigation show that there in the reactions of $\mathbf{1}^{-}$ is a gradual change from the characteristics of a pure ET reaction to those of a classical S_N2 reaction. This may be interpreted in two ways; the observation may be caused by the competition between two distinct reaction routes, ET and S_N2, with two types of TS, an outer-sphere dissociative ET followed by a radical coupling or a classical S_N2 TS; an alternative explanation is that there are transition states having structures with varying degrees of inner-sphere (bonding) stabilization ranging from the pure ET TS to the classical S_N2 TS. Although there is no definite evidence either way the fact that we find a linear dependence of ln k vs T^{-1} for all the substitution reactions we have investigated suggests that there is by this method no detectable shift in reaction path in this temperature interval. The observed difference in activation parameters would indicate that a break in the Arrhenius plot should be observed, at least if a change from ET to S_N2 occurred in a narrow temperature range.

If one defines any TS which is not a pure outer-sphere ET TS as an S_N2 TS then nearly all the reactions discussed here are S_N2 reactions. In analogy with the S_N2 - S_N1 and E1 - E2 - E1cb types of reaction it seems useful to have a special designation (e.g. S_{ET}/S_N2-hybrid) for reactions in the "grey" area between ET and S_N2 TS in which the TS has characteristics of both model reactions. A description of the criteria to place a given reaction in a suitable category could be to use k_{SUB}/k_{ET}, or activation parameters, or reactions with some racemization as a characteristicum for the "grey area", or something else; the most convenient criteria for an ET/S_N2-hybrid would probably be k_{SUB}/k_{ET}.

The results described above give hints on some of the important parameters which determine whether an ET, S_N2 or S_N1 type of reaction is likely to be favored. Besides the parameters, steric properties and standard potentials of the reaction partners, discussed below, other properties of the system influence the reaction route. Our results suggest with regard to potentials and steric properties (Ref. 15):

a) The S_N2 reaction is likely to take place, unless the steric hindrance prohibits an approach of the reagents to a distance at which some bonding stabilization can occur.

b) If the steric conditions prevent a bonding stabilization in the transition state and the driving force $\Delta G \leq 0$ then the ET reaction is likely to occur; the ET reaction is favored by a delocalized HOMO of the donor.

c) In the cases where steric factors inhibit the S_N2 reaction and ΔE is too positive to allow ET to proceed with a reasonable rate, then the classical S_N1 reaction may come into play by creating a planar carbocation R^+ with less steric hindrance than RX and which also is a much better electron acceptor than RX; this facilitates the bonding to the donor/nucleophile. Even then, if the nucleophile is very difficult to oxidize, equivalent of being a very poor electron donor, the S_N1 reaction may fail to occur; *e.g.* in aqueous solution anions as perchlorate or tetrafluoroborate are practically unreactive in an S_N1 reaction.

X-Philic reactions

In some aliphatic nucleophilic reactions with halogenated compounds the nucleophile attacks the halogen rather than the carbon, and the carbon is then a leaving group as a carbanion. The nucleophiles in such reactions are "soft", that is, they are easily oxidizable. Such X-philic (Ref. 16) reactions have been less investigated than the classical S_N2 reaction. A special type of X-philic reaction is the reductive elimination of *vic*-dihalides by iodide, in which iodine and an alkene is formed.

As such reactions proceed only when the nucleophile has a low oxidation potential it was of interest to investigate whether some X-philic reactions could proceed via an ET reaction with the transfer of an electron being the rate determining step.

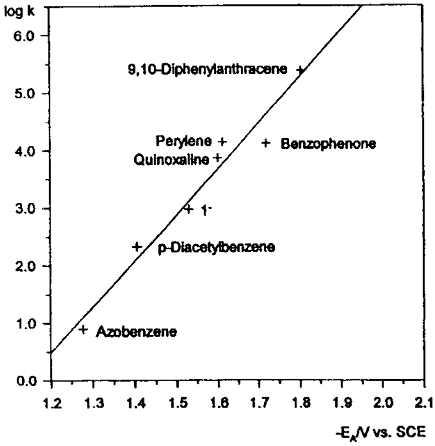


Fig. 5

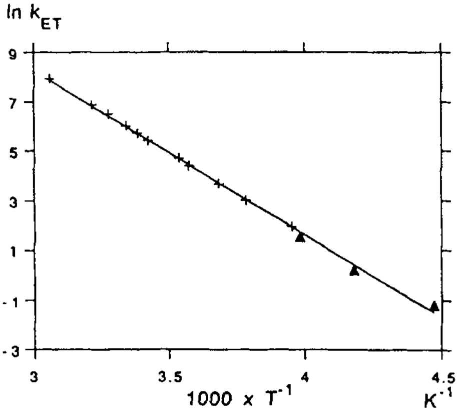


Fig. 6

The method used was similar to that described above; the rate constant of the ET from a series of aromatic radical anions to a given *vic*-dihalide was plotted against the oxidation potential of the radical anion and a straight line was drawn through the points; Fig. 5 shows such a plot for 1,2-dichloro-1,1,2,2-tetraphenylethane. The points of the rate constant for the reduction of the same dihalide by **1**$^-$ was found near the curve (Ref. 17). The rate-determining step was then assumed to be the transfer of an electron. The temperature dependence of the rate constant of the reaction between aromatic radical anions and *vic*-dihalides was measured (Ref. 18), and the linear correlation between ln *k* and T^{-1} was taken as an indication that the mechanism of the reductive elimination did not change in the temperature interval -50 °C to

50 °C. Fig. 6 shows the plot for the reaction between phenazine radical anion and 1,2-dichloro-1,1,2,2-tetraphenylethane. Furthermore, the values of the activation parameters, $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$, obtained showed that the same activation entropy and enthalpy was found in the nucleophilic substitution and the reductive elimination (Ref. 18). It remains to be seen whether other nucleophilic reactions may show examples of outer-sphere ET.

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