

Systematic Ranking of Nucleophiles as Electron Donors

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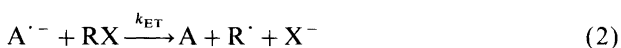
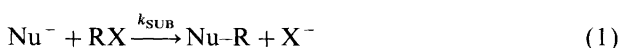
Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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A systematic ranking of different nucleophiles (including enolates, phenolates, thiophenolates, hydroxide, cyanide) with respect to their ability to stabilise the transition state of substitution reactions has been carried out in acetonitrile and dimethyl sulfoxide. The method is based on a comparison of the rate constant, k_{SUB} , for the substitution reaction between a given nucleophile and benzyl chloride with the rate constant, k_{ET} , for the corresponding electron transfer from an aromatic radical anion to benzyl chloride. The ratio $k_{\text{SUB}}/k_{\text{ET}}$ expresses the rate enhancement due to electronic interaction in the transition state, ΔG_{Sta} , of the substitution reaction. In this study, $k_{\text{SUB}}/k_{\text{ET}}$ ratios between 5 and 10^{31} were determined corresponding to ΔG_{Sta} -values of 4–175 kJ mol⁻¹. These values cover substitution reactions going from outer-sphere electron transfer to S_N2 with partial bond formation in the transition state. The $k_{\text{SUB}}/k_{\text{ET}}$ values are found to be largest for nucleophiles such as OH⁻ and CN⁻ with very poor electron-donating abilities (high oxidation potentials). When different types of nucleophile with similar oxidation potentials are compared, a decrease in $k_{\text{SUB}}/k_{\text{ET}}$ is observed going from sulfur- to carbon- and further to oxygen-centred nucleophiles. The ranking of nucleophiles in reactions involving electrophiles other than benzyl chloride is discussed with emphasis on steric hindrance and electronic effects.

Over the past 30 years electron transfer (ET) reactions have been suggested as important steps in many mechanisms. Different strategies have been developed to address this issue with most of them focusing on radical intermediates formed when a single electron is transferred between 'even-electron' donors and acceptors.^{1–4} The detection of radicals, however, does not imply that they are necessarily formed in the major reaction path if side reactions are possible. The reverse situation could also be envisioned in which a pair of radicals is formed by the ET reaction but the radicals are not detected because of a fast coupling reaction taking place within the solvent cage.

With the purpose of having a better description of the ET character in the transition state (TS) of substitution reactions, a kinetic method was developed in the 1980s.^{5–8} In particular, the work by Henning Lund extended the scope of this approach.⁹



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The method is based on a comparison of the rate constant for the substitution reaction [eqn. (1)] between a nucleophile Nu⁻ and a substrate/electrophile RX, k_{SUB} , with the corresponding ET rate constant, k_{ET} , obtained using an outer-sphere electron donor A^{·-} [eqn. (2)]. It is important that the standard potentials as well as the self-exchange reorganisation energies of the A/A^{·-} and Nu⁻/Nu⁻ couples are equal. The compounds normally used as electron donors are aromatic radical anions and metal complexes. If a $k_{\text{SUB}}/k_{\text{ET}}$ ratio of about 1 is measured for a given substitution process, the nucleophile reacts with the electrophile with a rate as expected for an outer-sphere ET reaction. Accordingly, the nucleophile can be classified as an outer-sphere electron donor in this specific reaction. On the other hand, if a significantly larger $k_{\text{SUB}}/k_{\text{ET}}$ value is obtained, the activation energy must be smaller for the substitution reaction than for the corresponding outer-sphere ET reaction. Thus, the substitution reaction proceeds by inner-sphere ET with strong electronic interaction between the two reactants in the TS. Within this framework a polar mechanism such as S_N2, in which a partial bond is formed between the nucleophilic and electrophilic centres in the TS, may be described as an inner-sphere ET.^{9–14}

In general, the activation energy for the substitution reaction (1), $\Delta G_{\text{SUB}}^\ddagger$, may be expressed as the difference between an outer-sphere ET activation energy, $\Delta G_{\text{ET}}^\ddagger$, and a stabilisation or interaction energy, ΔG_{Sta} , as stated in eqn. (3).

$$\Delta G_{\text{SUB}}^\ddagger = \Delta G_{\text{ET}}^\ddagger - \Delta G_{\text{Sta}} \quad (3)$$

$$\Delta G_{\text{ET}}^\ddagger = \Delta G_0^\ddagger \left(1 + \frac{\Delta G^\circ}{4\Delta G_0^\ddagger} \right)^2 \quad (4)$$

$$k_{\text{ET}} = Z \exp \left[\frac{-\Delta G_0^\ddagger}{RT} \left(1 - \frac{F(E_{\text{PhCH}_2\text{Cl}}^\circ - E_{\text{A/A}^\cdot}^\circ)}{4\Delta G_0^\ddagger} \right)^2 \right] \quad (5)$$

$$\Delta G_{\text{Sta}} = RT \ln(k_{\text{SUB}}/k_{\text{ET}}) \quad (6)$$

In the Marcus treatment of outer-sphere ET the stabilisation energy is assumed to be negligible but in practice an upper limit of 4 kJ mol⁻¹ is often used.¹⁵ The Marcus relation between $\Delta G_{\text{ET}}^\ddagger$ and the free energy of the reaction, ΔG° , is given in eqn. (4), where ΔG_0^\ddagger is the intrinsic barrier.^{15,16} According to Savéant this relationship is also adequate in the description of dissociative ET reactions.¹⁷ Expression (5) is derived by combining the Marcus and Eyring equations, in which Z is the collision frequency ($= 3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$), $E_{\text{A/A}^\cdot}^\circ$ the standard potential of the aromatic compound and $E_{\text{PhCH}_2\text{Cl}}^\circ$ the standard potential of benzyl chloride.* For a substitution process ΔG_{Sta} may be of a substantial magnitude owing to partial bond formation in the TS and Marcus theory cannot be applied *per se*. In fact, if the structure of the TS is assumed to be symmetric the stabilisation energy corresponds to one half of the bond energy of the new bond formed during the process. Since the present study is concerned with the formation of carbon-carbon, carbon-oxygen or carbon-sulfur bonds with bond strengths of up to ca. 350 kJ mol⁻¹, ΔG_{Sta} is expected to vary in the range 4–175 kJ mol⁻¹ for inner-sphere ET processes.

Experimentally, ΔG_{Sta} is quantified from the measured $k_{\text{SUB}}/k_{\text{ET}}$ ratios as stated in eqn. (6). This expression is easily obtained on the basis of TS theory and it shows that an inner-sphere ET reaction with ΔG_{Sta} in the range 4–175 kJ mol⁻¹ should be 5–10³¹ times faster than the corresponding outer-sphere ET. Still, outer-sphere ET may take place under appropriate conditions, for example, if a close approach between the two reactants and thus bond formation in the TS is prohibited by steric interference.²

In previous investigations of the ET character of substitution reactions, focus has been on reactions with $k_{\text{SUB}}/k_{\text{ET}}$ ratios in the range 1–10⁹.^{7,9,19,20} The major point was to relate the variation in $k_{\text{SUB}}/k_{\text{ET}}$ to the steric conditions at the electrophilic centre with almost no attention paid to the nucleophilic part. In this paper, the

* The reduction of benzyl chloride presumably follows the dissociative pathway¹⁸ and the standard potential $E_{\text{PhCH}_2\text{Cl}}^\circ$ is then defined according to the electrode process: $\text{PhCH}_2\text{Cl} + \text{e} \rightleftharpoons \text{PhCH}_2^\cdot + \text{Cl}^-$.

purpose is to describe in detail the role of the nucleophile and its features. In particular, we present a systematic ranking of nucleophiles in terms of their ability to stabilise the TS of substitution reactions. Benzyl chloride was chosen as the electrophile because of its high reactivity towards most anionic nucleophiles. Steric hindrance at the central primary carbon atom is small and most nucleophiles are free to approach the electrophilic centre to bonding distance without major geometric restrictions. Competing S_N1 or elimination reactions may also be disregarded. These features have so far allowed the measurement of k_{SUB} for a large number of nucleophiles as presented in Ref. 21 and more results are added in the present study. From the data, $k_{\text{SUB}}/k_{\text{ET}}$ values are obtained covering the whole accessible range of ratios from 1 to 10³¹.

Results and discussion

ET rate constants, k_{ET} , for the reaction between different aromatic radical anions and benzyl chloride were measured in acetonitrile and dimethyl sulfoxide (DMSO). The k_{ET} values are collected in Tables 1 and 2 and in Figs. 1 and 2 they are depicted as plots of $\log k_{\text{ET}}$ against the standard potential of the electron donors, $E_{\text{A/A}^\cdot}^\circ$. Although such plots should be parabolic according to

Table 1. Rate constants k_{ET} obtained for the reaction between different aromatic radical anions and benzyl chloride in acetonitrile–0.1 M Bu₄NBF₄ at 20 °C.

Mediator	$-E_{\text{A/A}^\cdot}^\circ/\text{V}^a$	$k_{\text{ET}}/\text{M}^{-1} \text{ s}^{-1}$	$\log k_{\text{ET}}$
Anthracene	1.974 ^b	9.5×10^4 ^b	4.98
9-Phenylanthracene	1.912	3.2×10^4	4.51
9,10-Diphenylanthracene	1.886	1.8×10^4	4.26
Benzophenone	1.754	1.5×10^3	3.18
Perylene	1.667	410	2.61
1,4-Dicyanobenzene	1.620 ^b	130	2.11
Azobenzene	1.332	2.8	0.45
Phenazine	1.168	0.11	-0.96
3-Nitrobenzophenone	0.998	2.3×10^{-2}	-1.64
Anthraquinone	0.882	1.0×10^{-3}	-3.00

^aVs. SCE. ^bFrom Ref. 21.

Table 2. Rate constants k_{ET} obtained for the reaction between different aromatic radical anions and benzyl chloride in DMSO–0.1 M Bu₄NBF₄ at 20 °C.

Mediator	$-E_{\text{A/A}^\cdot}^\circ/\text{V}^a$	$k_{\text{ET}}/\text{M}^{-1} \text{ s}^{-1}$	$\log k_{\text{ET}}$
Anthracene	1.852	8.1×10^4	4.91
9,10-Dimethylanthracene	1.793	5.1×10^4	4.71
9,10-Diphenylanthracene	1.760	2.2×10^4	4.34
Fluoranthene	1.632	2700	3.43
Perylene	1.572	940	2.97
Acenaphthylene	1.533	400	2.60
1,4-Dicyanobenzene	1.485	180	2.26
1,4-Diacetylbenzene	1.407	21	1.32
Phenazine	1.082	6.3×10^{-2}	-1.20
Anthraquinone	0.879	2.5×10^{-3}	-2.60

^aVs. SCE.

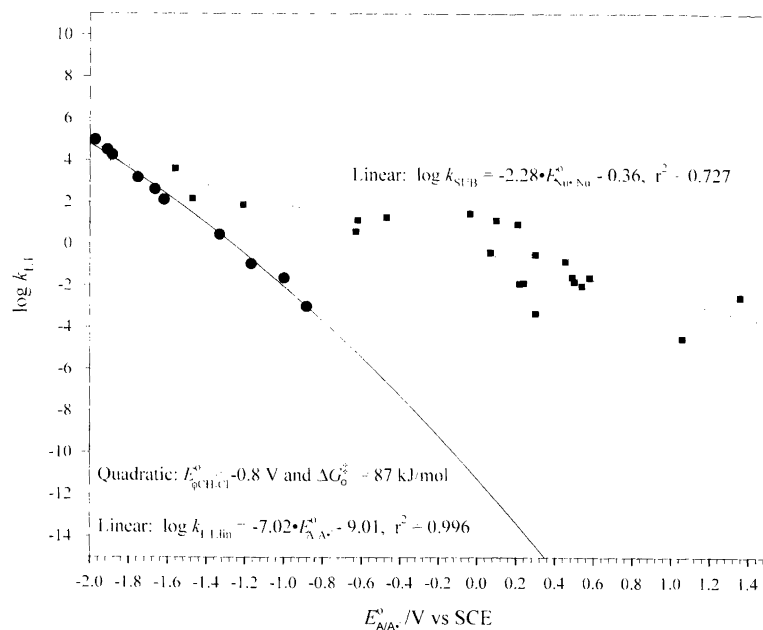


Fig. 1. Logarithm of the rate constant k_{ET} of the ET reaction between different aromatic radical anions and benzyl chloride versus the standard potential of the aromatic compounds $E_{A/A^{\cdot-}}^0$ in acetonitrile–0.1 M TBABF₄ (●). Linear (dashed line) and quadratic (solid curve) correlations are included. Data points ($E_{Nu^{\cdot-}/Nu}^0$, $\log k_{SUB}$) pertaining to the substitution reaction between different anionic nucleophiles and benzyl chloride are inserted (■) and the linear correlation obtained is shown as the straight dotted line.

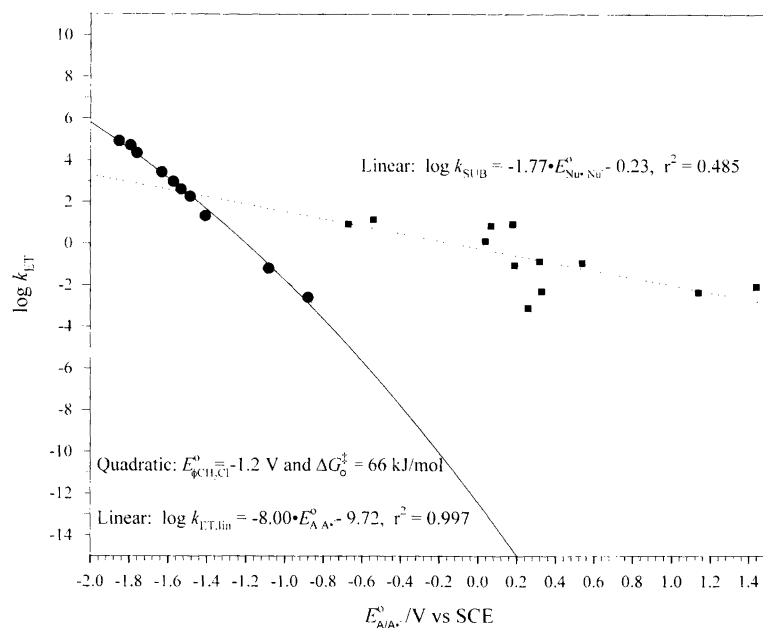


Fig. 2. Logarithm of the rate constant k_{ET} of the ET reaction between different aromatic radical anions and benzyl chloride versus the standard potential of the aromatic compounds $E_{A/A^{\cdot-}}^0$ in DMSO–0.1 M TBABF₄ (●). Linear (dashed line) and quadratic (solid curve) correlations are included. Data points ($E_{Nu^{\cdot-}/Nu}^0$, $\log k_{SUB}$) pertaining to the substitution reaction between different anionic nucleophiles and benzyl chloride are inserted (■) and the linear correlation obtained is shown as the straight dotted line.

eqn. (5), simple linear regression of the data points results in good fits indeed as shown by the dashed lines in the figures. The slopes found for acetonitrile and DMSO are -7.0 V^{-1} and -8.0 V^{-1} , respectively, which

by being multiplied by $-RT \ln 10/F$ are converted into slopes of $\Delta G_{ET}^{\ddagger}/\Delta G^{\circ} = 0.41$ and 0.47 .

The quadratic relationship (5) may also be fitted to the data points as illustrated by the solid curves in the

figures. Since the curvature is hardly discernible this enables only a rather crude estimation of $E_{\text{PhCH}_2\text{Cl}}^\circ$ and ΔG_0^\ddagger . For acetonitrile: $E_{\text{PhCH}_2\text{Cl}}^\circ = -0.8 \pm 0.1$ V vs. SCE, $\Delta G_0^\ddagger = 87 \pm 5$ kJ mol⁻¹ and for DMSO: $E_{\text{PhCH}_2\text{Cl}}^\circ = -1.2 \pm 0.1$ V vs. SCE, $\Delta G_0^\ddagger = 66 \pm 3$ kJ mol⁻¹. Actually, the above $E_{\text{PhCH}_2\text{Cl}}^\circ$ values are close to thermodynamically calculated values.¹⁸ The finding of large intrinsic barriers ΔG_0^\ddagger is also in accordance with expectation since the reduction process of benzyl chloride is accompanied by bond fragmentation of the relatively strong carbon–chlorine bond. Thus, on the present basis the parabolic relationship cannot be rejected and we decided to use both correlations in the further treatment of the kinetic data. Interestingly, for other electron acceptors such as bromides and in particular sulfides, the reduction of which is associated with a smaller intrinsic barrier, the situation is less ambiguous and here both distinct linear²² and parabolic relationships are observed.²³

The rate constant expected for a given substitution reaction, if it were to proceed by an ET process, may be obtained from either the linear or parabolic correlation by inserting the value of the standard potential of the nucleophile involved, $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ$. $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ$ is obtained in linear sweep voltammetry from the oxidative peak potential of Nu^- (see the Experimental for details).^{21,24–26} The thus calculated $k_{\text{ET,lin}}$ and $k_{\text{ET,par}}$ values are listed along with $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ$ in Tables 3 and 4.

The maximum difference between $k_{\text{ET,lin}}$ and $k_{\text{ET,par}}$ constitutes ‘only’ 40% as long as $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ$ is positioned within the potential interval of the aromatic mediators from -2.0 V to -0.8 V vs. SCE. Obviously, the difference becomes larger, if the correlations are applied outside this potential interval. For instance, when the rate constants are calculated at a potential of $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ = +1.2$ V, i.e. an extrapolation of 2 V from the nearest data point, the ratio is a factor of 10^8 . However, even such a factor is acceptable for our purpose considering that $k_{\text{SUB}}/k_{\text{ET}}$ ratios as high as 10^{31} may be anticipated for inner-sphere ET reactions in this region. Furthermore, it has no effect on the ranking of the different nucleophiles studied in this paper.

The rate constants, k_{SUB} , obtained for the substitution reactions of the nucleophiles with benzyl chloride are summarised in Tables 3 and 4 and in Figs. 1 and 2. The general feature of the k_{SUB} values is as described in Ref. 21, i.e. the more easily oxidisable anions with low values of $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ$ react faster with benzyl chloride. In fact, a rough linear correlation between $\log k_{\text{SUB}}$ and $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ$ exists with slopes of -2.3 V⁻¹ and -1.8 V⁻¹ for acetonitrile and DMSO, respectively, as indicated by the dotted straight lines in the figures. The scattering of the data points is quite significant and good to excellent correlations are obtained only if families of nucleophiles, in terms of carbon anions, oxygen anions or sulfur anions, are selected. This is not surprising since $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ$ expresses the readiness of the nucleophile to give up a single electron and it takes no specific electronic or structural properties of the two reactants into account,

which would be of major importance for inner-sphere ET reactions.

In the last two columns of Tables 3 and 4 the values of $k_{\text{SUB}}/k_{\text{ET}}$ and ΔG_{Sta} calculated from eqn. (6) are included.* The most profound feature of these is the increase observed as the electron-donating ability of the nucleophile is diminished, i.e. when $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ$ becomes higher. This is due to the fact that the sensitivity of the rate constant k_{SUB} towards $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ$ is much smaller compared with the influence of $E_{\text{A}^\circ/\text{A}^-}^\circ$ on k_{ET} . In fact, the slope difference of the two free energy plots of 5.5 ± 0.8 V⁻¹ corresponds to the slope of a $\log k_{\text{SUB}}/k_{\text{ET}}$ vs. E° plot. A straightforward interpretation of this behaviour is that while strongly electron-donating nucleophiles are able to transfer an electron to the electrophile from a long distance without efficient orbital overlap the nucleophiles with poorer electron-donating abilities need the stabilising effect of bond formation in the TS, i.e. a close approach to the electrophile, in order to react at all.

The solvent effect on $k_{\text{SUB}}/k_{\text{ET}}$ is relatively small with a tendency to increase on going from acetonitrile to DMSO as illustrated by the results obtained for fluorenone, 4-methoxythiophenolate, thiophenolate, 4-nitrothiophenolate, phenolate, hydroxide and cyanide. Ion-pairing effects are also believed to be of minor importance, since tetrabutylammonium from the supporting electrolyte is the counter ion of the anionic nucleophiles in most cases.³⁰ For fluorenone the effect of using K^+ as counter ion was studied (entries 4 and 5, Table 3). Interestingly, $E_{\text{Nu}^\circ/\text{Nu}^-}^\circ$ is found to be unaffected while k_{SUB} and the $k_{\text{SUB}}/k_{\text{ET}}$ ratio are increased. This points to a much stronger interaction of K^+ with the developing chloride in the TS than with the delocalised fluorenone in the initial state.

In Fig. 3, a selection of nucleophiles is ranked according to the $k_{\text{SUB}}/k_{\text{ET}}$ and ΔG_{Sta} values obtained in acetonitrile and DMSO on the basis of the quadratic approach. The nucleophiles cover almost the whole accessible range of $k_{\text{SUB}}/k_{\text{ET}}$ ratios from 1 to 10^{31} , going from outer-sphere ET to $\text{S}_{\text{N}}2$ reactions with partial bond formation in the TS. The largest $k_{\text{SUB}}/k_{\text{ET}} = 1.9 \times 10^{31}$ is found for the reaction in DMSO between CN^- and benzyl chloride yielding benzyl cyanide in an exothermic process. According to eqn. (6) this corresponds to a ΔG_{Sta} of 175 kJ mol⁻¹, which is 50 kJ mol⁻¹ below half of the bond dissociation energy of the C–CN bond in benzyl cyanide (≈ 450 kJ mol⁻¹). As discussed in the introduction, such high values of $k_{\text{SUB}}/k_{\text{ET}}$ and ΔG_{Sta} are close to

* For a few nucleophiles such as hydroxide and cyanide the $k_{\text{SUB}}/k_{\text{ET}}$ ratio should be considered as a minimum value since the self-exchange reorganisation energy of the OH^-/OH^- and CN^-/CN^- couples is somewhat higher than of $\text{A}^\circ/\text{A}^-$.^{4,20} Previous studies have also shown that the ET reaction between A^- and sterically non-hindered electrophiles may possess some inner-sphere character and not be truly outer-sphere.^{11,22,27–29} This effect would lower systematically the $k_{\text{SUB}}/k_{\text{ET}}$ ratios obtained but not influence the ranking of nucleophiles.

Table 3. Rate constants k_{SUB} for the substitution reaction between various anionic nucleophiles (with the standard potential $E_{\text{Nu}^{\ominus}/\text{Nu}^-}$) and benzyl chloride in acetonitrile–0.1 M Bu_4NBF_4 at 20 °C. Expected ET rate constants calculated from linear ($k_{\text{ET,lin}}$) and parabolic ($k_{\text{ET,par}}$) fits are included as well as the $k_{\text{SUB}}/k_{\text{ET}}$ ratio and ΔG_{Sta} .

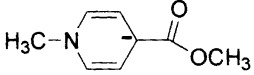
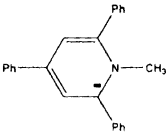
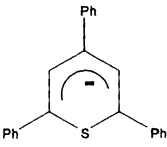
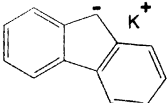
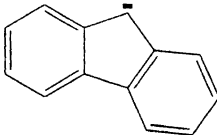
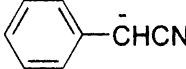
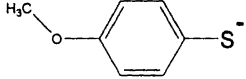
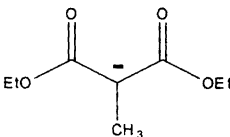
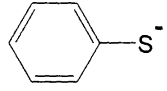
Structure and name of Nu: ^{−a}	$k_{\text{SUB}}/\text{M}^{-1} \text{s}^{-1}$	$E_{\text{Nu}^{\ominus}/\text{Nu}^-}/\text{V}^b$	$k_{\text{ET,lin}}/\text{M}^{-1} \text{s}^{-1}$ $k_{\text{ET,par}}/\text{M}^{-1} \text{s}^{-1}$	$k_{\text{SUB}}/k_{\text{ET,lin}}$ $k_{\text{SUB}}/k_{\text{ET,par}}$	$\Delta G_{\text{Sta}}/\text{kJ mol}^{-1}$
 1,4-Dihydro-4-methoxycarbonyl-1-methylpyridine anion	$4.1 \times 10^3{}^c$	$-1.563{}^c$	90 1.3×10^2	45 32	9.3 8.4
 1-Methyl-2,4,6-triphenylpyridine anion	$1.5 \times 10^2{}^c$	$-1.473{}^c$	21 32	7.1 4.8	4.8 3.8
 2,4,6-Triphenylthiopyran anion	$76{}^c$	$-1.210{}^c$	0.30 0.40	2.5×10^2 1.9×10^2	13 13
 Fluorenone	$14{}^d$	$-0.62{}^c$	2.2×10^{-5} 5.7×10^{-6}	6.4×10^5 2.5×10^6	33 36
 Fluorenone	$4.0{}^e$	$-0.63{}^c$	2.6×10^{-5} 7.0×10^{-6}	1.6×10^5 5.7×10^5	29 32
 Cyanophenylmethanide	$19{}^f$	$-0.46{}^f$	1.6×10^{-6} 2.0×10^{-7}	1.2×10^7 9.6×10^7	40 45
 4-Methoxythiophenolate	$29{}^d$	$-0.035{}^g$	1.9×10^{-9} 1.5×10^{-11}	1.6×10^{10} 1.9×10^{12}	57 69
 Diethyl methylmalonate anion	$0.40{}^f$	$0.08{}^f$	2.7×10^{-10} 8.4×10^{-13}	1.5×10^9 4.8×10^{11}	51 66
 Thiophenolate	$14{}^d$	$0.10{}^g$	1.9×10^{-10} 5.2×10^{-13}	7.2×10^{10} 2.7×10^{13}	61 75

Table 3. (Continued.)

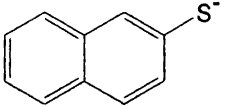
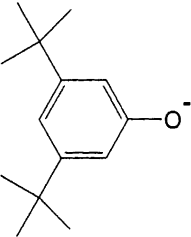
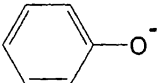
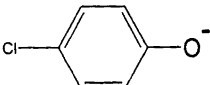
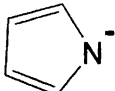

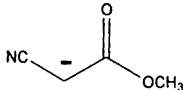
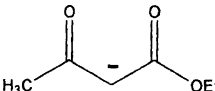
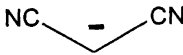
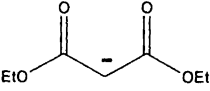
Structure and name of Nu: ^{-a}	$k_{\text{SUB}}/\text{M}^{-1} \text{s}^{-1}$	$E_{\text{Nu}^{\cdot-}/\text{Nu}^-}/\text{V}^b$	$k_{\text{ET,lin}}/\text{M}^{-1} \text{s}^{-1}$ $k_{\text{ET,par}}/\text{M}^{-1} \text{s}^{-1}$	$k_{\text{SUB}}/k_{\text{ET,lin}}$ $k_{\text{SUB}}/k_{\text{ET,par}}$	$\Delta G_{\text{Sta}}/\text{kJ mol}^{-1}$
 2-Naphthalenethiolate	9.3 ^f	0.20 ^f	3.9×10^{-11} 4.3×10^{-14}	2.4×10^{11} 2.2×10^{14}	64 80
 3,5-Di-tert-butylphenolate	1.3×10^{-2f}	0.23 ^f	2.4×10^{-11} 2.0×10^{-14}	5.5×10^8 6.4×10^{11}	49 66
 Phenolate	1.4×10^{-2f}	0.24 ^h	2.0×10^{-11} 1.6×10^{-14}	7.0×10^8 8.8×10^{11}	50 67
 4-Chlorophenolate	4.8×10^{-4f}	0.30 ⁱ	7.6×10^{-12} 3.5×10^{-15}	6.3×10^7 1.4×10^{11}	44 63
 Pyrrolate anion	0.32 ^f	0.31 ^f	6.5×10^{-12} 2.7×10^{-15}	4.9×10^{10} 1.2×10^{14}	60 79
 4-Nitrothiophenolate	0.15 ^d	0.455 ^g	6.3×10^{-13} 6.1×10^{-17}	2.4×10^{11} 2.5×10^{15}	64 86
 Cyano(methoxycarbonyl)methanide	2.6×10^{-2f}	0.50 ^f	3.0×10^{-13} 1.9×10^{-17}	8.6×10^{10} 1.4×10^{15}	61 85
 Ethyl acetoacetate anion	1.6×10^{-2f}	0.51 ^f	2.6×10^{-13} 1.4×10^{-17}	6.2×10^{10} 1.1×10^{15}	61 84
 Dicyanomethanide	1.0×10^{-2f}	0.55 ^f	1.4×10^{-13} 4.8×10^{-18}	7.4×10^{10} 2.1×10^{15}	61 86
 Bis(ethoxycarbonyl)methanide	2.5×10^{-2f}	0.59 ^f	7.1×10^{-14} 1.6×10^{-18}	3.5×10^{11} 1.5×10^{16}	65 91

Table 3. (Continued.)

Structure and name of Nu: ^{-a}	$k_{\text{SUB}}/\text{M}^{-1} \text{s}^{-1}$	$E_{\text{Nu}^{\cdot-}/\text{Nu}^-}/\text{V}^b$	$k_{\text{ET,lin}}/\text{M}^{-1} \text{s}^{-1}$ $k_{\text{ET,par}}/\text{M}^{-1} \text{s}^{-1}$	$k_{\text{SUB}}/k_{\text{ET,lin}}$ $k_{\text{SUB}}/k_{\text{ET,par}}$	$\Delta G_{\text{Sta}}/\text{kJ mol}^{-1}$
OH ⁻ Hydroxide	3.0×10^{-5j}	1.06^k	3.6×10^{-17} 2.5×10^{-24}	8.5×10^{11} 1.2×10^{19}	67 107
CN ⁻ Cyanide	2.9×10^{-3j}	1.36^k	2.8×10^{-19} 2.6×10^{-28}	1.0×10^{16} 1.1×10^{25}	90 140

^aTetrabutylammonium salt if nothing else is indicated. ^bVs. SCE. ^cCyclic or linear sweep voltammetric measurements. ^dStopped-flow UV measurement. ^eDip-probe UV measurement. ^fFrom Ref. 21. The kinetic shift of $E_{\text{ox,p}}$ relative to $E_{\text{Nu}^{\cdot-}/\text{Nu}^-}$ is estimated to be -0.101 V on the basis of eqn. (7). ^gFrom Ref. 25. ^hFrom Ref. 26. ⁱInterpolated from the Hammett relationship given in Ref. 26. ^jMonitored by ^1H NMR. ^kFrom Ref. 4, pp. 47 and 62.

the upper limits of the two scales. The reactions of OH⁻ and thiophenolates are also characterised by substantial $k_{\text{SUB}}/k_{\text{ET}}$ values in the order of 10^{15} – 10^{25} . The smallest ratio of 4.8 is found for the anion of 1-methyl-2,4,6-triphenylpyridine, a highly delocalised and strongly electron-donating nucleophile.

It is also interesting to compare the ΔG_{Sta} values for C-, O- and S-centred nucleophiles with similar oxidation potentials. For instance, in the case of diethyl methylmalonate anion and thiophenolate (entries 8 and 9, Table 3) ΔG_{Sta} is higher for the latter by about 10 kJ mol^{-1} . Similarly, 2-naphthalenethiolate is a better

inner-sphere ET donor with a higher ΔG_{Sta} of 15 kJ mol^{-1} compared with 3,5-di-*tert*-butylphenolate (entries 10 and 11, Table 3). Thus, the general ranking of nucleophiles in terms of their ability to stabilise the transition state is $\text{RS}^- > \text{R}_3\text{C}^- > \text{RO}^-$, i.e. the same as their order of reactivity.²¹ Traditionally, this is explained by the high polarisability of RS^- which allows it to bring a greater degree of electron density to the substrate than the smaller nucleophiles whose electron clouds are held more tightly; that $\text{R}_3\text{C}^- > \text{RO}^-$ is attributed to the higher basicity of the former anion. An interesting aspect of our comparison is that it is carried out for nucleophiles

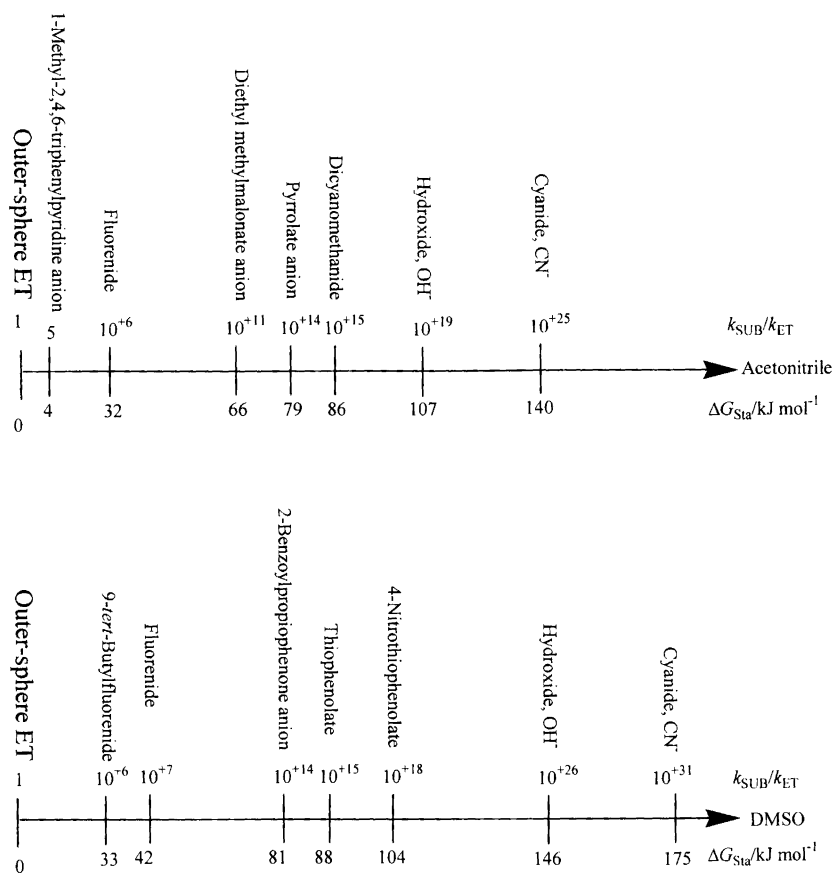


Fig. 3. Ranking of a selection of nucleophiles with respect to values of $k_{\text{SUB}}/k_{\text{ET}}$ and ΔG_{Sta} obtained in the quadratic approach for the substitution reaction with benzyl chloride.

Table 4. Rate constants for the substitution reaction between various anionic nucleophiles (with the standard potential $E_{\text{Nu}^{\ominus}/\text{Nu}^-}^{\ominus}$) and benzyl chloride in DMSO–0.1 M Bu_4NBF_4 at 20 °C. Expected ET rate constants calculated from linear ($k_{\text{ET,lin}}$) and parabolic ($k_{\text{ET,par}}$) fits are included as well as the $k_{\text{SUB}}/k_{\text{ET}}$ ratio and ΔG_{Sta} .

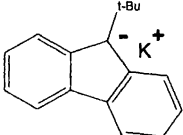
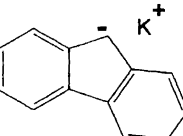
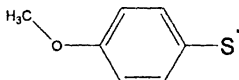
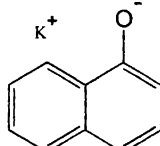
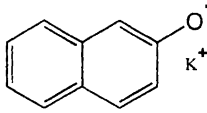
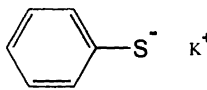
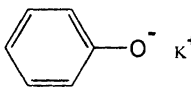
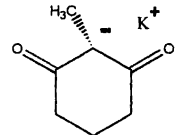
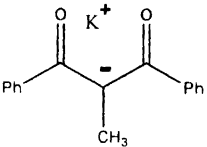
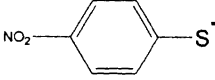
Structure and name of Nu^{-a}	$k_{\text{SUB}}/\text{M}^{-1} \text{s}^{-1}$	$E_{\text{Nu}^{\ominus}/\text{Nu}^-}^{\ominus}/\text{V}^b$	$k_{\text{ET,lin}}/\text{M}^{-1} \text{s}^{-1}$ $k_{\text{ET,par}}/\text{M}^{-1} \text{s}^{-1}$	$k_{\text{SUB}}/k_{\text{ET,lin}}$ $k_{\text{SUB}}/k_{\text{ET,par}}$	$\Delta G_{\text{Sta}}/\text{kJ mol}^{-1}$
 9- <i>tert</i> -Butylfluorenone ^c	8.6 ^d	−0.67 ^e	4.4×10^{-5} 1.2×10^{-5}	2.0×10^5 7.2×10^5	30 33
 Fluorenone ^f	14 ^d	−0.54 ^e	4.0×10^{-6} 5.4×10^{-7}	3.5×10^6 2.6×10^7	37 42
 4-Methoxythiophenolate ^g	1.3 ^d	0.05 ^h	7.6×10^{-11} 8.9×10^{-14}	1.7×10^{10} 1.5×10^{13}	57 74
 1-Naphtholate ⁱ	7.1 ^d	0.07 ^j	5.2×10^{-11} 5.0×10^{-14}	1.4×10^{11} 1.4×10^{14}	62 79
 2-Naphtholate ^k	9.1×10^{-2d}	0.18 ^l	6.9×10^{-12} 2.0×10^{-15}	1.3×10^{10} 4.5×10^{13}	57 77
 Thiophenolate ^m	8.7 ^d	0.18 ^h	6.9×10^{-12} 2.0×10^{-15}	1.3×10^{12} 4.3×10^{15}	68 88
 Phenolate ⁿ	0.14 ^d	0.32 ^o	5.3×10^{-13} 3.0×10^{-17}	2.7×10^{11} 4.6×10^{15}	64 88
 2-Methylcyclohexane-1,3-dione anion	7.9×10^{-4p}	0.26 ^q	1.6×10^{-12} 1.9×10^{-16}	5.0×10^8 4.2×10^{12}	49 71

Table 4. (Continued.)

Structure and name of Nu ^{-a}	$k_{\text{SUB}}/\text{M}^{-1} \text{s}^{-1}$	$E_{\text{Nu}^{\ominus}/\text{Nu}^-}/\text{V}^b$	$k_{\text{ET,lin}}/\text{M}^{-1} \text{s}^{-1}$ $k_{\text{ET,par}}/\text{M}^{-1} \text{s}^{-1}$	$k_{\text{SUB}}/k_{\text{ET,lin}}$ $k_{\text{SUB}}/k_{\text{ET,par}}$	$\Delta G_{\text{Sta}}/\text{kJ mol}^{-1}$
 2-Benzoylpropiophenone anion	5.1×10^{-3p}	0.33 ^r	4.4×10^{-13} 2.2×10^{-17}	1.2×10^{10} 2.3×10^{14}	56 81
 4-Nitrothiophenolate ^s	0.12 ^d	0.54 ^h	9.1×10^{-15} 3.1×10^{-20}	1.3×10^{13} 3.9×10^{18}	74 104
OH ⁻ Hydroxide	4.5×10^{-3t}	1.14 ^u	1.5×10^{-19} 3.5×10^{-29}	3.1×10^{16} 1.3×10^{26}	93 146
CN ⁻ Cyanide	8.5×10^{-3t}	1.44 ^u	5.8×10^{-22} 4.5×10^{-34}	1.5×10^{19} 1.9×10^{31}	108 175

^aTetrabutylammonium salt if nothing else is indicated. ^bVs. SCE. ^cOrange, $\lambda_{\text{max}}=478$ nm. ^dDip-probe UV measurement. ^eFrom Ref. 24. ^fOrange, $\lambda_{\text{max}}=477$ nm. ^gPale green, $\lambda_{\text{max}}=345$ nm. ^hFrom Ref. 25 and shifted 0.08 V because of solvent change. ⁱPale green, $\lambda_{\text{max}}=348$ nm. ^j $E_{\text{ox,p}}=0.00$ V vs. SCE at $\nu=1$ V s⁻¹, $C_0=3.2$ mM, k_{DIM} assumed to be equal to 10^9 M⁻¹ s⁻¹. Kinetic shift in a DIM1 mechanism = 0.069 V. ^kGreen, $\lambda_{\text{max}}=390$ nm. ^l $E_{\text{ox,p}}=0.11$ V vs. SCE at $\nu=1$ V s⁻¹, $C_0=3.9$ mM, k_{DIM} assumed to be equal to 10^9 M⁻¹ s⁻¹. Kinetic shift in a DIM1 mechanism = 0.071 V. ^mPale green, $\lambda_{\text{max}}=328$ nm. ⁿPale green, $\lambda_{\text{max}}=328$ nm. ^oFrom Ref. 26 but shifted 0.08 V because of solvent change. ^pMonitored by linear sweep voltammetry. ^q $E_{\text{ox,p}}=0.20$ V vs. SCE at $\nu=1$ V s⁻¹, $C_0=1.6$ mM, k_{DIM} assumed to be equal to 10^9 M⁻¹ s⁻¹. Kinetic shift in a DIM1 mechanism = 0.063 V. $E_{\text{ox,p}}=0.274$ V vs. SCE at $\nu=1$ V s⁻¹, $C_0=0.84$ mM, k_{DIM} assumed to be equal to 10^9 M⁻¹ s⁻¹. Kinetic shift in a DIM1 mechanism = 0.058 V. ^rRed, $\lambda_{\text{max}}=500$ nm. ^tMonitored by ¹H NMR. ^uFrom Ref. 4, pp. 47 and 62 and shifted a further 0.08 V because of solvent change.

of similar $E_{\text{Nu}^{\ominus}/\text{Nu}^-}$ values, or expressed differently, the energy of the initial state is the same. In contrast, the energy of the final state (substitution product + leaving group) is dependent on the energy of the new bond formed. Unfortunately, the differences in the strength of carbon–sulfur, carbon–carbon and carbon–oxygen bonds³¹ are too small to conclude for certain whether a relationship between the development in ΔG_{Sta} and the C–Nu bond strength is present.

In principle, all substitution reactions studied herein follow the inner-sphere ET mechanism with $\Delta G_{\text{Sta}} > 4$ kJ mol⁻¹. Previous studies employing stereochemical probes have shown that even a modest stabilisation of ca. 10 kJ mol⁻¹ (or $k_{\text{SUB}}/k_{\text{ET}} \approx 100$) should be sufficient to prevent the formation of radical intermediates.^{9,19,22,32,33} At that point, bond formation between the electron donor and the electrophile is so developed in the TS that the reaction proceeds by inversion at the central carbon and not by racemisation as seen for outer-sphere ET. In this sense, substitution reactions may be classified as S_N2 processes when $k_{\text{SUB}}/k_{\text{ET}} > 100$ or $\Delta G_{\text{Sta}} > 10$ kJ mol⁻¹. According to Figs. 1 and 2, this implies that the S_N2 mechanism is expected to prevail for benzyl chloride when it is involved in reactions with nucleophiles of $E_{\text{Nu}^{\ominus}/\text{Nu}^-} > -1.4$ V vs. SCE; a result in line with the conclusions presented in Ref. 21. Note that no specific steric effects are taken into consideration in the above discussion since benzyl chlor-

ide essentially has no steric constraints. However, in particular cases this is not completely correct as illustrated by the results obtained for the nucleophiles 9-*tert*-butylfluorenyl and fluorenyl (entries 1 and 2, Table 4), where the latter has a higher reactivity as expected due to its much less sterically hindered nature and despite its less negative $E_{\text{Nu}^{\ominus}/\text{Nu}^-}$ value.

The main advantage of the $k_{\text{SUB}}/k_{\text{ET}}$ approach is that it gives a quantitative measure of the electronic interaction in the TS and provides a description of substitution processes even if they appear to be alike at first glance from a stereochemical point of view. In this respect, the approach is also a better tool than the use of activation entropies ΔS^\ddagger .^{22,27} For inner-sphere ET the geometrical requirements of the TS are stricter compared with outer-sphere ET and more negative ΔS^\ddagger values are expected. However, the differences in ΔS^\ddagger vanish as $\Delta G_{\text{Sta}} > 10$ kJ mol⁻¹ and a detailed description of inner-sphere ET reactions can therefore not be obtained by this procedure.

Once a ranking of nucleophiles in terms of $k_{\text{SUB}}/k_{\text{ET}}$ has been accomplished as in the reaction of benzyl chloride, it becomes possible to predict when to expect inversion or partial racemisation in substitution reactions of these nucleophiles with other electrophiles. We propose that the ranking of nucleophiles presented above is valid also for other primary electrophiles although the absolute ΔG_{Sta} scale will be different. For instance, if 4-cyano-

benzyl chloride with its higher reduction potential were used as the electrophile rather than benzyl chloride the electron-accepting ability would be increased while leaving the steric conditions at the electrophilic centre essentially unchanged. According to the free energy plots in Figs. 1 and 2, both the standard ET and the substitution reaction would then be expected to proceed faster with the latter process exhibiting a somewhat weaker potential dependence. Thus, the $k_{\text{SUB}}/k_{\text{ET}}$ ratio and ΔG_{Sta} for a given nucleophile should diminish and substitution reactions involving nucleophiles with $E_{\text{Nu}^{\circ}/\text{Nu}^-}^{\circ} < -1.4$ V vs. SCE would certainly be expected to have $k_{\text{SUB}}/k_{\text{ET}} < 100$ for which partial racemisation takes place. A similar effect should be observed if a better leaving group such as bromide rather than chloride were introduced at the electrophilic centre.

If the electrophile becomes more sterically hindered than benzyl chloride, the steric conditions at the nucleophilic site are obviously going to play a much larger role and deviations from the general ranking listed above are expected. Some indications of how the $k_{\text{SUB}}/k_{\text{ET}}$ and ΔG_{Sta} values are affected when benzyl chloride is α -substituted by alkyl groups may be found in a previous study carried out in *N,N*-dimethylformamide.²⁷ While k_{ET} is affected only to a minor extent, k_{SUB} decreases substantially because a close approach of the nucleophile to the electrophile becomes difficult and in some cases even is prevented. The result is a large decrease of the $k_{\text{SUB}}/k_{\text{ET}}$ ratio. For instance, in the reaction of the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine ($E_{\text{Nu}^{\circ}/\text{Nu}^-}^{\circ} = -1.530$ V vs. SCE in *N,N*-dimethylformamide) $k_{\text{SUB}}/k_{\text{ET}}$ decreases from 83 to 0.8 going from benzyl chloride to (1-chloro-2,2-dimethylpropyl)benzene as the electrophile.²⁷ Stereochemically, the former reaction is predicted to proceed by nearly complete inversion, while the latter should be characterised by racemisation. A rough estimate of the potential, at which $k_{\text{SUB}}/k_{\text{ET}} = 100$ and changeover in mechanism occurs for (1-chloro-2,2-dimethylpropyl)benzene, is $E_{\text{Nu}^{\circ}/\text{Nu}^-}^{\circ} = -1.0$ V vs. SCE, a value higher by 0.4 V compared with the benzyl chloride system. On the other hand, if $E_{\text{Nu}^{\circ}/\text{Nu}^-}^{\circ}$ becomes too high, the inner-sphere ET is not expected to occur at all for sterically hindered compounds since the substitution rate simply becomes too small. Elimination and $\text{S}_{\text{N}}1$ -like reactions then provide alternative pathways. In the rate-controlling first step of the $\text{S}_{\text{N}}1$ reaction the electrophile is dissociated to yield a carbonium ion stabilised by the electron-donating alkyl groups. In this manner, the electron-accepting ability is increased along with a release of the steric hindrance at the electrophilic centre and the attack of the nucleophile becomes possible in the second step.

Experimental

Reagents. The supporting electrolyte, Bu_4NBF_4 , was prepared by standard procedures. Acetonitrile was distilled from P_2O_5 and subsequently K_2CO_3 . Just prior to

use it was dried through a column containing activated alumina. DMSO (Aldrich) was stored under nitrogen (Sure Seal bottles) and used without further purification. All handling of DMSO was performed on a vacuum line using normal syringe techniques. Benzyl chloride, aromatic mediators, tetrabutylammonium hydroxide (40% w/w), tetrabutylammonium cyanide and most of the precursors of the nucleophiles (fluorene, *p*-methoxythiophenol, *p*-nitrothiophenol, thiophenol, phenol, 1-naphthol, 2-naphthol) were commercially available and used as received. The preparation of 4-methoxycarbonyl-1-methylpyridinium perchlorate, 1-methyl-2,4,6-triphenylpyridinium perchlorate and 2,4,6-triphenylthiopyrylium perchlorate has been described previously.³⁴ The corresponding nucleophiles were generated during cyclic voltammetry by a two step reversible reduction of the cations. 9-*tert*-Butylfluorene was synthesised as described in Ref. 24. Most of the anionic nucleophiles in DMSO were prepared by deprotonating Nu-H with the base dimethylpotassium ($\text{CH}_3\text{SOCH}_2\text{K}$) using the procedure of Olmstead *et al.*³⁵ In acetonitrile, fluorenyl was also generated electrochemically by reduction of 9-phenoxyfluorene. 4-Nitrothiophenolate in DMSO and all 4-substituted thiophenolates in acetonitrile were electro-synthesised by reduction of the corresponding bis(4-substituted phenyl) disulfides.³⁶ The parent compounds were prepared according to Drabowicz and Mikolajczyk.³⁷

Instrumentation. NMR spectra were recorded on a Varian Gemini 200 MHz spectrometer. The electrochemical equipment and data handling procedures have been described previously.³⁸ A description of the electrochemical stopped-flow and dip-probe systems may be found in Ref. 39.

Procedures. Most of the anionic nucleophiles exhibit irreversible oxidation waves during cyclic voltammetry, even at scan rates as high as 100 V s^{-1} . The irreversible peak oxidation potentials were measured relative to the ferrocenium/ferrocene redox pair, the standard potential of which is +0.410 and +0.430 V vs. SCE in acetonitrile and DMSO, respectively. Previous studies of 9-substituted fluorenyls have shown that the electrode reaction follows a DIM1 mechanism, in which the dimerisation of the radicals formed after oxidation of the anionic substrate at the electrode proceeds at a rate close to the diffusion-controlled limit. The only exception is when the substituent is large and bulky such as *tert*-butyl.²⁴ In the present study the following slopes were found for almost all of the nucleophiles investigated in support of the DIM1 mechanism:⁴⁰ $dE_{\text{ox,p}}/d \log \nu \approx 20 \text{ mV}$ and $dE_{\text{ox,p}}/d \log C_0 \approx -20 \text{ mV}$, where $E_{\text{ox,p}}$ is the irreversible peak oxidation potential, ν is the sweep rate and C_0 the concentration of the nucleophile. In the case of diethyl methylmalonate anion in DMSO, however, the two slopes obtained (28 and 0 mV, respectively) were very different from the above values and the nucleophile was

not included in Table 4. The oxidation peak potentials were converted to standard potentials by inserting the experimental parameters into eqn. (7).⁴¹

$$E_{\text{Nu}^{\circ}/\text{Nu}}^{\circ} = E_{\text{ox,p}} - \frac{RT}{F} 0.902 + \frac{RT}{3F} \ln \left(\frac{2RTk_{\text{DIM}}C_{\text{o}}}{3Fv} \right) \quad (7)$$

The rate constant of dimerisation k_{DIM} was assumed in general to be $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $10^9 \text{ M}^{-1} \text{ s}^{-1}$ for acetonitrile and DMSO, respectively.^{24,25}

The methods used for measuring k_{ET} have been described previously.³⁸ As regards the determination of k_{SUB} , cyclic voltammetry was used for the first three nucleophiles listed in Table 3.⁷ When the anionic nucleophiles were coloured, stopped-flow or dip-probe experiments were normally employed.^{39,42} The reaction of non-coloured nucleophiles (deprotonated 2-methylcyclohexane-1,3-dione and 2-benzoylpropiophenone) was monitored by measuring the peak oxidation current in linear sweep voltammetry at a fixed sweep rate. All experiments were conducted with an excess of benzyl chloride in order to achieve pseudo first order conditions.

¹H NMR spectroscopy was used to monitor the slow reactions of HO^- and CN^- with benzyl chloride. The reaction between HO^- and benzyl chloride was carried out in an NMR-tube by mixing 400 mM $\text{Bu}_4\text{N}^+\text{OH}^-$ and 40 mM benzyl chloride in deuteriated solvents of acetonitrile or DMSO. The disappearance of the peak at $\delta_{\text{H}} = 4.76$ (2 H, s, PhCH_2Cl) and appearance of the new peak at $\delta_{\text{H}} = 4.66$ (2 H, s, PhCH_2OH) were followed for 48 h. For the reaction between CN^- and benzyl chloride in deuteriated acetonitrile, 400 mM $\text{Bu}_4\text{N}^+\text{CN}^-$ was mixed with 40 mM benzyl chloride. The disappearance of the peak at $\delta_{\text{H}} = 4.76$ (2 H, s, PhCH_2Cl) and appearance of the new peak at $\delta_{\text{H}} = 3.99$ (2 H, s, PhCH_2CN) were followed. In DMSO the reaction was faster and carried out under second order conditions by mixing 40 mM of both reactants.

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