

Electrochemical Measurements of Rate Constants for the Electron Transfer Reaction to Sterically Hindered Alkyl Halides

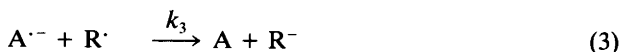
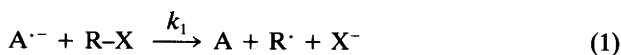
Kim Daasbjerg, Steen U. Pedersen and Henning Lund

Department of Organic Chemistry, University of Aarhus, DK-8000 Århus C, Denmark

Daasbjerg, K., Pedersen, S. U. and Lund, H., 1989. Electrochemical Measurements of Rate Constants for the Electron Transfer Reaction to Sterically Hindered Alkyl Halides. – Acta Chem. Scand. 43: 876–881.

Rate constants (k_1) have been measured for electron transfer from different electron donors to *t*-butyl chloride, neopentyl bromide, *exo*-norbornyl bromide, isobornyl bromide, bornyl bromide and adamantyl bromide. The electron donors are typically anion radicals of aromatic or heteroaromatic compounds, where the unpaired electron is delocalized over a large π -electron system. Curves showing the relationship between the logarithm of k_1 and the potential of the electron donor are also included. Rate constants have been measured for the substitution reaction between the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (1^-) and the six alkyl halides. The rate constant (k_{SUB}) for the substitution reaction of 1^- on the alkyl halide is compared with k_{SET} , which is the rate constant for an ET reaction of a hypothetical electron donor with the same standard potential as $1^-/1^\cdot$. The $k_{\text{SUB}}/k_{\text{SET}}$ values show that all these reactions are ET-like and the order of $k_{\text{SUB}}/k_{\text{SET}}$ is the same as the order of steric hindrance of the alkyl halides.

The outer-sphere electron transfer (ET) reaction between electron donors and alkyl halides has been studied intensively over the last decades.¹⁻¹⁰ Electrochemistry has been used to establish the mechanism and to measure the rate constant of this ET reaction:

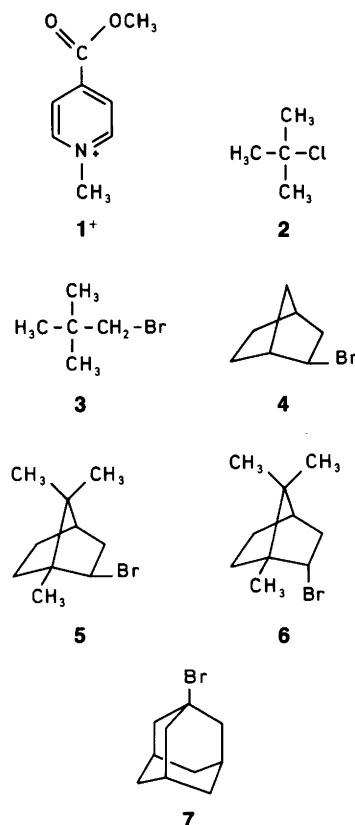


$A-R^-$ and R^- will either be protonated or will react with the substrate in a nucleophilic way. The ET reaction (1) is irreversible because of the concerted R–X bond cleavage.¹¹

The competition between coupling (2) and reduction (3) has been treated in a recent paper.¹² It was found that reduction (3) occurs, when $E^\circ_{A^{\cdot-}/A}$ is more negative than $E_{R^\cdot/R}$.

Linear-sweep voltammetry (LSV) and cyclic voltammetry (CV) have previously been used to measure k_1 , whereas the competition parameter, $q = k_3/(k_2+k_3)$, has been determined by coulometry and LSV.^{7,8,13,14} LSV and CV are both limited by a minimum scan-rate of 20 mV s⁻¹. If lower scan rates are applied, the mass transfer will not be purely diffusional as assumed in the digital simulation. The lower limit of the scan-rate sets a lower limit to the measurable rate constant in ET reactions. This limit in k_1 is equal to 1 M⁻¹ s⁻¹.

Very recently a new method was presented for measuring k_1 values for slow reactions ($k_1 < 10 \text{ M}^{-1} \text{ s}^{-1}$).¹⁵ The lower limit of measurable k_1 values is here $1 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. This method is also advantageous because the measurement of k_1 is independent of the q value which is not the case for the other techniques.



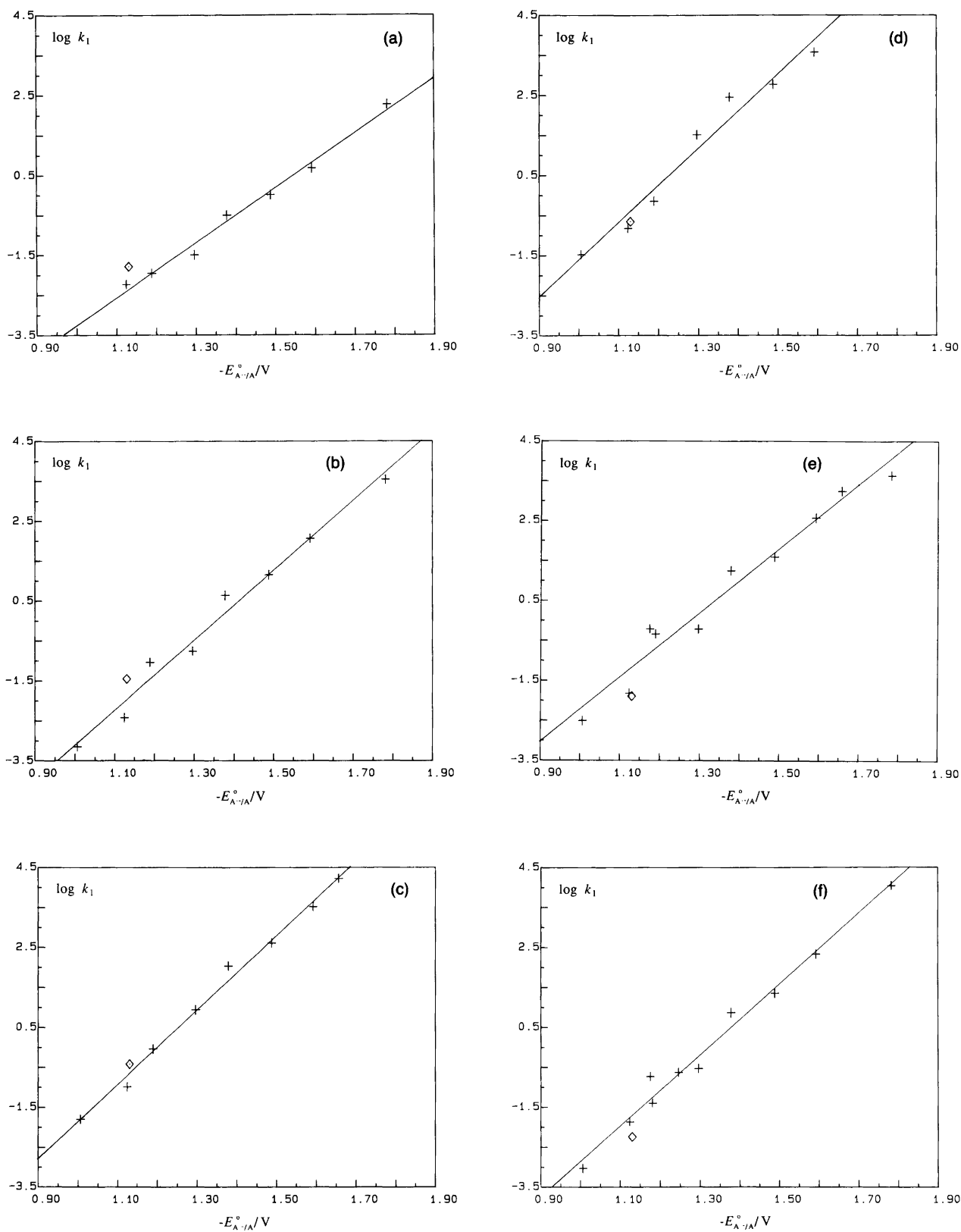


Fig. 1. Rate of electron transfer, k_1 , from some electrochemically generated anion radicals (+) and 1^- (\diamond) to sterically hindered alkyl halides: (a) *t*-butyl chloride, (b) neopentyl bromide, (c) *exo*-norbornyl bromide, (d) isobornyl bromide, (e) bornyl bromide, (f) adamantyl bromide, in DMF/TBABF₄ (0.1 M) at 22°C.

Table 1. Rate constants for electron transfer from electrochemically generated anion radicals to some sterically hindered alkyl halides in DMF/0.1 M TBABF₄, measured potentiostatically at ultramicroelectrodes or by cyclic voltammetry (*T* = 22 °C).

| BX | A | $-E_{A^{\cdot-}/A}/V^c$ | $k_{SET}/M^{-1}s^{-1}$ | $\log k_{SET}$ |
|------------------------------|---------------------------|-------------------------|------------------------|----------------|
| <i>t</i> -Butyl chloride | Acridine | 1.124 | 0.00580 ^b | -2.24 |
| | Perylene | 1.189 | 0.0109 ^b | -1.96 |
| | Benzophenone | 1.296 | 0.0237 ^b | -1.63 |
| | 9,10-Diphenylanthracene | 1.378 | 0.31 ^b | -0.51 |
| | Anthracene | 1.488 | 1.00 ^b | 0.00 |
| | Pyrene | 1.592 | 4.67 ^{a 3} | 0.67 |
| | Chrysene | 1.782 | 183 ^{a 3} | 2.26 |
| Neopentyl bromide | <i>p</i> -Diacetylbenzene | 1.006 | 0.000712 ^b | -3.15 |
| | Acridine | 1.124 | 0.00382 ^b | -2.42 |
| | Perylene | 1.189 | 0.12 ^b | -0.92 |
| | Benzophenone | 1.296 | 0.22 ^b | -0.66 |
| | 9,10-Diphenylanthracene | 1.378 | 4.34 ^{a 3} | 0.64 |
| | Anthracene | 1.488 | 14 ^{a 3} | 1.15 |
| | Pyrene | 1.592 | 116 ^{a 3} | 2.06 |
| Chrysene | 1.782 | 3440 ^{a 3} | 3.54 | |
| <i>exo</i> -Norbonyl bromide | <i>p</i> -Diacetylbenzene | 1.006 | 0.0159 ^b | -1.80 |
| | Acridine | 1.124 | 0.102 ^b | -0.99 |
| | Perylene | 1.189 | 0.92 ^b | -0.04 |
| | Benzophenone | 1.296 | 8.70 ^a | 0.94 |
| | 9,10-Diphenylanthracene | 1.378 | 107 ^a | 2.03 |
| | Anthracene | 1.488 | 410 ^a | 2.61 |
| | Pyrene | 1.592 | 3330 ^a | 3.52 |
| Quinoline | 1.656 | 17000 ^a | 4.22 | |
| Isobornyl bromide | <i>p</i> -Diacetylbenzene | 1.006 | 0.0330 ^b | -1.48 |
| | Acridine | 1.124 | 0.15 ^b | -0.83 |
| | Perylene | 1.189 | 4.0 ^b | 0.60 |
| | Benzophenone | 1.296 | 32 ^a | 1.51 |
| | 9,10-Diphenylanthracene | 1.378 | 281 ^a | 2.45 |
| | Anthracene | 1.488 | 590 ^a | 2.77 |
| | Pyrene | 1.592 | 3710 ^a | 3.57 |
| Bornyl bromide | <i>p</i> -Diacetylbenzene | 1.006 | 0.00306 ^b | -2.51 |
| | Acridine | 1.124 | 0.0151 ^b | -1.82 |
| | Quinoxaline | 1.175 | 0.62 ^b | -0.21 |
| | Perylene | 1.189 | 0.46 ^b | -0.34 |
| | Benzophenone | 1.296 | 0.62 ^b | -0.21 |
| | 9,10-Diphenylanthracene | 1.378 | 18 ^a | 1.25 |
| | Anthracene | 1.488 | 40 ^a | 1.60 |
| | Pyrene | 1.592 | 383 ^a | 2.58 |
| | Quinoline | 1.656 | 1760 ^a | 3.25 |
| Chrysene | 1.782 | 4410 ^a | 3.64 | |
| Adamantyl bromide | <i>p</i> -Diacetylbenzene | 1.006 | 0.000936 ^b | -3.03 |
| | Acridine | 1.124 | 0.0135 ^b | -1.87 |
| | Acenaphthylene | 1.181 | 0.0402 ^b | -1.40 |
| | Quinoxaline | 1.175 | 0.19 ^b | -0.73 |
| | 9,10-Diacetoxanthracene | 1.246 | 0.23 ^b | -0.63 |
| | Benzophenone | 1.296 | 0.29 ^b | -0.53 |
| | 9,10-Diphenylanthracene | 1.378 | 7.34 ^{a 3} | 0.87 |
| | Anthracene | 1.488 | 22.50 ^{a 3} | 1.35 |
| | Pyrene | 1.592 | 212 ^{a 3} | 2.33 |
| | Chrysene | 1.782 | 10800 ^{a 3} | 4.03 |

^aObtained by cyclic voltammetry. ^bObtained by the potentiostatic method at an ultramicroelectrode. ^cMeasured against the Ag/AgI, I⁻ = 0.10 M reference electrode.

This paper presents k_1 values for reactions of different electron donors with *t*-butyl chloride (2), neopentyl bromide (3), *exo*-norbonyl bromide (4), isobornyl bromide

(5), bornyl bromide (6) and adamantyl bromide (7). The electron donors are typically anion radicals of aromatic or heteroaromatic compounds, where the unpaired electron is

delocalized over a large π -electron system. Curves showing the relationship between the logarithm of k_1 and the standard potential of the electron donor are also included.

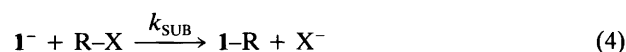
Finally, k_{SUB} values are measured for the substitution reaction between the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine ($\mathbf{1}^-$) and the six alkyl halides. The measured k_{SUB} values are compared with k_1 values for an ET reaction of an electron donor with the same redox potential as $\mathbf{1}^-/\mathbf{1}^-$.

Results and discussion

Values of the rate constant k_1 were measured for ET-reactions between a number of electron donors and the six sterically hindered alkyl halides. The k_1 values are given in Table 1, and the logarithm of k_1 is plotted against the standard potential of the electron donors in Figs. 1(a)–(f). These plots should be parabolic according to the Marcus theory,^{16–18} whereas Grimshaw *et al.*¹⁹ postulate a linear relationship between the logarithm of k_1 and the standard potentials of the donors $E_{\text{A}^-/\text{A}^\cdot}^\circ$. The experimental data presented here cover too narrow a potential range to exhibit a decisive curvature. We thus decided to make the best straight line from the experimental points by linear least-squares analysis. These lines are included in the plots, Figs. 1(a)–(f). In this procedure a rejection of the Marcus theory is not implied.

Two points representing benzophenone, $E_{\text{A}^-/\text{A}^\cdot}^\circ = -1.296$ V, and quinoxaline, $E_{\text{A}^-/\text{A}^\cdot}^\circ = -1.175$ V, vs. Ag/AgI deviate somewhat from the lines in some of the plots and this trend has been observed before: k_{SET} for quinoxaline is higher than expected and k_{SET} for benzophenone is lower. The presence of heteroatoms in the two compounds will polarize the electron density which might influence the rate. If the reaction has a component of inner-sphere ET ($\text{S}_{\text{N}}2$ -like) both compounds should react faster than expected for an outer-sphere ET. In that case the deviation should be more pronounced in the reaction with primary alkyl halides such as 1-bromobutane and this has not been observed. Neither do the differences in the solvent reorganization energies, γ , for the anion-radicals of aromatic hydrocarbons and for the anion radicals of quinoxaline and benzophenone seem to be the explanation. A higher γ -value is expected for species with a higher localization of the negative charge. This could explain the behaviour of benzophenone but leaves the behaviour of quinoxaline as an open question.

The rate constants k_{SUB} for the substitution reactions between $\mathbf{1}^-$ and the six alkyl halides according to reaction (4) have been measured. The procedure for measuring k_{SUB}



for $\mathbf{1}^-$ is the same as for measuring k_1 for the anion radicals. $\mathbf{1}^+\text{ClO}_4^-$ is reduced by two electrons to $\mathbf{1}^-$. The concentration of $\mathbf{1}^-$ is monitored by an ultramicroelectrode at a potential between $E_{\mathbf{1}^-/\mathbf{1}^\cdot}^\circ$ and $E_{\mathbf{1}^\cdot/\mathbf{1}^+}^\circ$. The logarithm of the

Table 2. Rate constants for the substitution reaction between the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine ($\mathbf{1}^-$) and some sterically hindered alkyl halides in DMF/0.1 M TBABF measured potentiostatically at ultramicroelectrodes ($T = 22^\circ\text{C}$).

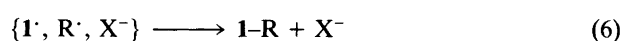
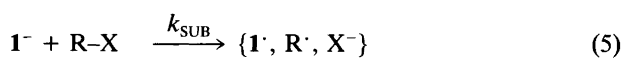
| BX | $k_{\text{SUB}}/\text{M}^{-1} \text{s}^{-1}$ | $k_{\text{SET}}/\text{M}^{-1} \text{s}^{-1}$ | $k_{\text{SUB}}/k_{\text{SET}}$ |
|-------------------------------|--|--|---------------------------------|
| <i>t</i> -Butyl chloride | 0.0164 | 0.00395 | 4.15 |
| Neopentyl bromide | 0.0357 | 0.0112 | 3.19 |
| <i>exo</i> -Norbornyl bromide | 0.38 | 0.22 | 1.73 |
| Isobornyl bromide | 0.22 | 0.55 | 0.40 |
| Bornyl bromide | 0.0129 | 0.0642 | 0.20 |
| Adamantyl bromide | 0.00577 | 0.0197 | 0.29 |

current, $\ln(i)$, is plotted vs. time (t); the slope is equal to $k_{\text{SUB}}[\text{R-X}]$. The k_{SUB} values obtained are given in Table 2. The k_{SUB} values for **3** and **7** have previously been measured by polarography to be 2.9×10^{-2} and $1.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, respectively,³ but we believe that the new results 3.6×10^{-2} and $5.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, respectively, are more correct. The redox potential of $\mathbf{1}^-$ is -1.13 V vs. Ag/AgI. The points $\log k_{\text{SUB}}$, $E_{\mathbf{1}^-/\mathbf{1}^\cdot}^\circ$ are included in Figs. 1(a)–(f).

The anion $\mathbf{1}^-$ has previously been shown to react as a nucleophile and as an electron donor. It was of interest to investigate the nature of the reaction between $\mathbf{1}^-$ and sterically hindered alkyl halides. The classical theory for $\text{S}_{\text{N}}2$ reactions predicts that the $\text{S}_{\text{N}}2$ reaction is slowed down or blocked by steric hindrance. With sufficient steric hindrance, the rate of the substitution reaction drops to a level equal to that expected for a pure ET reaction.

The measured k_{SUB} values for each of the six alkyl halides were compared with the k_{SET} values for an electron donor of the same redox potential as $\mathbf{1}^-$. In practice $\log(k_{\text{SET}})$ values were obtained from the curves in Figs. 1(a)–(f) at $E_{\text{A}^-/\text{A}^\cdot}^\circ$ equal to -1.13 V. The $k_{\text{SUB}}/k_{\text{SET}}$ values are included in Table 2.

A value of the ratio between 0.2 and 5 is taken as evidence for an ET reaction mechanism, eqns. (5) and (6).



Here eqn. (5) is the rate-determining ET step. The species in the brackets are thought to be in a solvent cage. The radicals will only under very special conditions be able to leave the solvent cage as free radicals. A large value of $k_{\text{SUB}}/k_{\text{SET}}$ as is found, for example, for the reaction of $\mathbf{1}^-$ with 1-bromobutane ($k_{\text{SUB}}/k_{\text{SET}} = 400^3$) indicates greater stabilization of the transition state by concerted bond formation than in pure ET reactions. The stabilization leads to a higher rate constant. The $\text{S}_{\text{N}}2$ process is characterized by a concerted bond-forming/bond-breaking process. The rate constant for an $\text{S}_{\text{N}}2$ reaction will always be higher than the equivalent rate constant of an equivalent pure ET-reaction.

The $k_{\text{SUB}}/k_{\text{SET}}$ values indicate that the substitution reaction of 1^- with **6** is more ET-like than the reaction between 1^- and **4**. The result is in accordance with results from preparative reductions,²⁰ where the reduction of 1^- and **6** gave a coupling product containing approximately equal amounts of the two isomers (1.4:1.0) as expected for a pure ET reaction, whereas the reaction between 1^- and **4** leads to a significant excess of one isomer (3:1). A pure S_N2 reaction is expected to proceed cleanly with inversion to give one isomer.

The $k_{\text{SUB}}/k_{\text{SET}}$ ratios found for the six sterically hindered alkyl halides are all small indicating a substantial degree of ET and only a small bonding stabilization in the transition state. In fact, we find that many of the ratios are less than 1. We believe that this is an artefact caused by several factors and that k_{SET} is the minimum rate constant for a substitution reaction. At least three factors could lead to $k_{\text{SUB}}/k_{\text{SET}}$ values being too small: (a) anion-radicals of aromatic or heteroaromatic compounds might not act as pure electron donors; (b) neglect of the possible curvature in the $\log k_1$ vs. $E_{\text{A}^-/\text{A}}$ lines; (c) k_{SET} values found from the curves are not necessarily representative for an ET reaction of 1^- . The $\log k_1$ vs. $E_{\text{A}^-/\text{A}}$ curves are based on the assumption that the self-reorganisation energies for the electron donor, $\lambda_{\text{D}}(0)$, for aromatic and heteroaromatic compounds are small (ca. 10 kcal mol⁻¹) and their variations negligible compared with the $\lambda_{\text{A}}(0)$ -value for the electron acceptor, the alkyl halides. The overall λ value $\{\lambda = 1/2[\lambda_{\text{D}}(0) + \lambda_{\text{A}}(0)]\}$ will then be practically constant for all the reactions on the curve. We have not so far been able to measure $\lambda_{\text{D}}(0)$ for $1^-/1^-$ and consequently we do not know if the approximation made for the anion radicals is valid for 1^- .

The $k_{\text{SUB}}/k_{\text{SET}}$ ratios of the alkyl halides, **2-7**, decrease with increased steric hindrance, with **2** being the least and **7** the most sterically hindered alkyl halide.

Conclusions

The sterically hindered alkyl halides, **2-7**, react slowly with 1^- leading to substitution. The $k_{\text{SUB}}/k_{\text{SET}}$ values indicate that the transition state is very ET-like in accordance with the assumption that the shift from an S_N2 to an ET reaction is strongly promoted by steric hindrance. The results for e.g. **4** and **6** indicate that even for reactions of low $k_{\text{SUB}}/k_{\text{SET}}$ ratio, there are differences which are manifested in the stereochemistry of the products.

Experimental

Reagents. The supporting electrolyte, Bu_4NBF_4 , and solvent, DMF (Fluka AG), were purified by standard procedures. 4-Methoxycarbonyl-1-methylpyridinium perchlorate was obtained by quaternization of methyl isonicotinoate with dimethyl sulfate in acetonitrile at 40 °C for 20 h; on addition of diethyl ether a layer separated which was dissolved in water. A saturated aqueous solution of sodium perchlorate was added and the precipitate was filtered; it

was recrystallized from acetonitrile/diethyl ether. The other electron donors were commercially available and used as received. *exo*-Norbornyl bromide,²¹ bornyl bromide,²² and isobornyl bromide²³ were synthesized according to the references given. The hydrogen bromide was prepared as in Ref. 24. The spectral data obtained for the three compounds showed no impurities. *t*-Butyl chloride, 1-adamantyl bromide and neopentyl bromide are commercially available and were used as received. No electroactive impurities could be detected by CV.

Instrumentation. The platinum disk ultramicroelectrode of diameter 10 μm was prepared according to the instructions in Ref. 25. The electrode was polished with diamond paste (0.25 micron). The reference electrode was a silver wire in $\text{TBABF}_4/\text{DMF}$. The potentiostat and recording system have been described elsewhere.¹⁵

Procedure. The procedure for measuring the k_1 values for anion radicals of aromatic or heteroaromatic compounds and alkyl halides has been described in detail in Ref. 15. The procedure for measuring k_{SUB} for 1^- and alkyl halides is quite similar. The major difference is that two electrons are consumed in the reduction of 1^+ to 1^- and that the potential for monitoring was chosen such that it was between $E_{1^-/1^-}$ and $E_{1^+/1^+}$. 1^- is rather sensitive to oxidation by oxygen.

The standard potentials of the aromatic compounds, $E_{\text{A}^-/\text{A}}$, were measured relative to the first reduction peak of anthraquinone. The standard potential of anthraquinone has been measured previously as -0.40 V vs. Ag/AgI , 1^- .

References

1. Simonet, J., Michel, M.-A. and Lund, H. *Acta Chem. Scand., Ser. B* 29 (1975) 489.
2. Lund, T. and Lund, H. *Tetrahedron Lett.* 27 (1986) 95.
3. Lund, T. and Lund, H. *Acta Chem. Scand., Ser. B* 40 (1986) 470.
4. Lund, T., Pedersen, S. U., Lund, H., Ming, C. K. and Utley, J. H. P. *Acta Chem. Scand., Ser. B* 41 (1987) 285.
5. Gatti, N., Pedersen, S. U. and Lund, H. *Acta Chem. Scand., Ser. B* 42 (1988) 11.
6. Andrieux, C. P., Gallardo, I., Savéant, J.-M. and Su, K. B. *J. Am. Chem. Soc.* 108 (1986) 638.
7. Savéant, J.-M. and Su, K. B. *J. Electroanal. Chem.* 196 (1985) 1.
8. Nadjo, L., Savéant, J.-M. and Su, K. B. *J. Electroanal. Chem.* 196 (1985) 23.
9. Savéant, J.-M. *Bull. Soc. Chim. France* 2 (1988) 225.
10. Lexa, D., Savéant, J.-M., Su, K. B. and Wang, D. L. *J. Am. Chem. Soc.* 110 (1988) 7617.
11. Savéant, J.-M. *J. Am. Chem. Soc.* 109 (1987) 6788.
12. Fuhlendorf, R., Occhialini, D., Pedersen, S. U. and Lund, H. *Acta Chem. Scand., Ser. B* 43 (1989) 803.
13. Pedersen, S. U. and Svensmark, B. *Acta Chem. Scand., Ser. A* 40 (1986) 607.
14. Pedersen, S. U. *Acta Chem. Scand., Ser. A* 41 (1987) 391.
15. Pedersen, S. U. and Daasbjerg, K. *Acta Chem. Scand., Ser. B* 43 (1989) 301.

16. Marcus, R. A. *J. Chem. Phys.* 24 (1956) 966.
17. Ebersson, L. *Adv. Phys. Org. Chem.* 18 (1982) 79.
18. Ebersson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer Verlag, Heidelberg 1987.
19. Grimshaw, J., Langan, J. R. and Salmon, G. A. *J. Chem. Soc., Chem. Commun.* (1988) 1115.
20. Daasbjerg, K., Lund, T. and Lund, H. *Tetrahedron Lett.* 30 (1989) 493.
21. Roberts, J. D., Trumbull, E. R., Bennett, W. and Armstrong, R. *J. Am. Chem. Soc.* 72 (1950) 3329.
22. Wallach, O. *Liebigs Ann. Chem.* 239 (1887) 1.
23. Semmler, F. W. *Ber. Deutsch. Chem. Ges.* 33 (1900) 3420.
24. Duncan, D. R. *Inorg. Synth.* 1 (1939) 151.
25. Fleischmann, M., Pons, S., Rolison, D. R. and Schmidt, P. P. *Ultramicroelectrodes*, Datatech. Systems Inc., Morgantown 1987.

Received March 28, 1989.