EPR-Spectroscopic Investigation of the Self-Exchange Electron Transfer Rate Constants and Reorganization Energies for some Electrochemically Generated Radicals

Dorothée Jürgen,[a] Steen Uttrup Pedersen,[a] Jens Arne Pedersen[b] and Henning Lund[a,*]

[a]Department of Organic Chemistry and [b]Department of Physical Chemistry, University of Århus, DK-8000 Århus C, Denmark

Jürgen, D., Pedersen, S. U., Pedersen, J. A. and Lund, A., 1997. EPR-Spectroscopic Investigation of the Self-Exchange Electron Transfer Rate Constants and Reorganization Energies for some Electrochemically Generated Radicals. – Acta Chem. Scand. 51: 767–772. © Acta Chemica Scandinavica 1997.

The electron transfer rate constants for self-exchange reactions between 4-methoxycarbonyl-1-methylpyridinium cation (1^+) and its radical ($1^{\cdot}$), azulene (2) and azulene radical anion ($2^{-\cdot}$) and 2,5-di-*tert*-butyl-1,4-dimethoxybenzene (3) and its radical cation ($3^{+\cdot}$) have been investigated by EPR line-broadening measurements in DMF or acetonitrile. The aromatic radicals were generated electrochemically in an improved flow cell. The rate constants were determined in the slow exchange region, and the self-exchange reorganization energies were calculated.

The role of electron transfer (ET) in aliphatic nucleophilic substitution has been the subject of theoretical and experimental investigations for the last two decades.[1] It has been suggested that whereas most aliphatic nucleophilic substitutions follow a polar route some reactions between electron-rich anions and sterically hindered alkyl halides involve an outer-sphere ET with the ET being the rate-determining step.[2]

For the latter kind of investigation three types of experiment have been used as arguments: kinetic,[3–6] stereochemical[7] and thermodynamic.[8] In the kinetic line of argument the rate of ET, measured by use of CV or LSV, between a series of supposedly outer-sphere electron donors (radical anions of aromatic and heteroaromatic compounds) and a given alkyl halide, was compared with the rate of ET from an electron-rich anion to the same alkyl halide. In a comparison of electron transfer rates it is necessary to know that the reorganization energies λ connected with the ET reactions are similar. According to the Marcus cross-relation the self-exchange reorganization energy for the nucleophile/electron donor should be similar to the self-exchange reorganisation energy for the aromatic electron donor. The alkyl halide is the same in both these experiments and therefore the contribution from this to the reorganisation energies cancel.

A number of data have been published for the rate constants of self-exchange ET reactions. Most investigations have been on the exchange between neutral parent compounds and their radical anions [eqn. (1)]. Szwarc *et al.*[9] and Eberson[10] give a good review of the work done until 1982. After that mainly Grampp *et al.*[11–13] and Larsen *et al.*[14,15] have worked on this topic.

$$A + A^{-\cdot}/A^{-\cdot} + A \qquad (1)$$

The data available of ET reactions between neutral parent compounds and their radical cations [eqn. (2)] are very limited. A collection of values is found in papers by Eberson,[10] Bard *et al.*[16] and Grampp *et al.*[17] This is supplemented by the work of Fuhlendorff *et al.*[18] and Goez.[19]

$$A + A^{+\cdot}/A^{+\cdot} + A \qquad (2)$$

Few neutral radicals are persistent enough for convenient measurement of the rate of their self-exchange ET reaction, and only three rate constants for self-exchange ET reactions involving neutral radicals [eqns. (3) and (4)] have been reported. Rate constants are known for the reactions between tris-(*p*-nitrophenyl)methyl radical and its anion,[20] triphenylmethyl radical and its cation,[21] and 9-phenylacridinyl radical and its cation.[22]

$$A^{\cdot} + A^+/A^+ + A^{\cdot} \qquad (3)$$

$$A^{\cdot} + A^-/A^- + A^{\cdot} \qquad (4)$$

The present work is concerned with measurements of λ-values of exchange reactions of the four types [eqns.

---

(1)–(4)]. 4-Methoxycarbonyl-1-methylpyridinium cation (1^+), the radical ($1^·$) and the anion (1^-) [eqns. (3) and (4)] have been extensively used as nucleophile/electron donors in the investigations of the ET vs. polar reactions in the aliphatic nucleophilic substitution.[2-8] The electron exchange between azulene (2) and its radical anion ($2^{-·}$) was of interest to investigate whether the λ-value of a non-benzoid hydrocarbon with unusual photochemical properties (the fluorescence is an $S_2 \rightarrow S_0$ transition), differed from that of the isomeric naphthalene. The exchange reaction between 2,5-di-tert-butyl-1,4-dimethoxybenzene (3) and its radical cation ($3^{+·}$) was of interest for its use in indirect oxidations and the measurements of ET in such reactions. Attempts were also made to measure the rate constant for the exchange reaction between $1^·$ and 1^-. EPR-spectra of $1^·$,[23] $2^{-·}$[24] and $3^{+·}$[25] have been published.

COOCH₃

CH₃O

OCH₃

CH₃

N
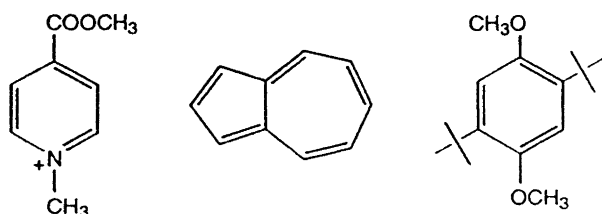
Scheme 1.

The rate constant k_{ET} can be determined from the line-broadening of the EPR signals, when the radical concentration is held constant and the concentration of the parent compound [A_i] is varied.[26,27] The slow exchange limit, which is characterized by no line overlap in the spectrum, was mostly used in this work. In this limit each line in the EPR spectrum of the radical is broadened in proportion to the concentration of the parent aromatic compound. The rate constant $k_{ET,obs}$ (obs = observed) can be calculated from this line broadening ($\Delta B_i - \Delta B_0$), where ΔB_i and ΔB_0 are the linewidths for a given concentration of parent compound [A_i] and at zero concentration of A [A_0], respectively [eqn. (5)].

$$k_{ET,obs} = \frac{1}{\tau[A_i]} = \frac{\pi\sqrt{3}\gamma(\Delta B_i - \Delta B_0)}{P[A_i]} \tag{5}$$

γ is the gyromagnetic ratio of the electron (= $2.83 \times 10^6 \, G^{-1} s^{-1}$), τ is the lifetime of the radical and P is a normalization factor for the broadening of the lines in the EPR spectrum.

As the radicals examined in this investigation were relatively unstable, they were generated in an electrochemical flow cell. Waller et al.[28] give a review about the different in situ and some ex situ methods which can be used for electrochemical EPR experiments. With the in situ methods it is more difficult to obtain a homogeneous solution in the EPR cavity and thus to control the radical concentration. Therefore the ex situ methods are preferred for self-exchange measurements.

Results and discussion

The corrected linewidths (Lw) were plotted against the concentration of the parent aromatic compound [A_i] at a radical concentration of 0.1 mM in the case of $2/2^{-·}$ and $1^+/1^·$ and 0.052 mM for $3/3^{+·}$ (Fig. 1). The observed rate constant $k_{ET,obs}$ was determined from the slope according to eqn. (6).

$$Lw = \frac{\Delta B_i}{P} = \frac{\Delta B_0}{P} + \frac{k_{ET,obs}}{1.525 \times 10^7}[A_i] \tag{6}$$

For $1^+/1^·$ and $2/2^{-·}$ a correction for diffusion was necessary according to eqn. (7). The rate constant for diffusion k_d in DMF was obtained from the Smoluchovski equation $k_d = 8RT/3\eta$, with η = viscosity of DMF. From the literature[29,30] k_d was found to be $(0.73 \pm 0.04) \times 10^{10} \, M^{-1} s^{-1}$ at 293 ± 1 K. The self-reorganization energies were calculated according to eqn. (8) with the collision frequency Z[31,32] equal to $10^{11} \, M^{-1} s^{-1}$.

$$\frac{1}{k_{ET}} = \frac{1}{k_{ET,obs}} - \frac{1}{k_d} \tag{7}$$

$$\lambda = -4RT \ln \frac{k_{ET}}{Z} \tag{8}$$

The results were obtained in DMF or acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. In view of the results of Ward[33] ion-pairing in such polar solvents with large ions should not present a problem.

The results obtained are collected in Table 1. For the reaction of $2/2^{-·}$ the rate constant $k_{ET} = 7.7 \times 10^8 \, M^{-1} s^{-1}$ and the self-reorganization energy $\lambda = 11.3 \, kcal \, mol^{-1}$. These values are well within the range of published data for radical anions in DMF.[10,14,15] For example carbocyclic compounds such as anthracene and diphenylanthracene have rate constants $k_{ET} = 1.5 \times 10^9 \, M^{-1} s^{-1}$ and $1.1 \times 10^9 \, M^{-1} s^{-1}$, respectively.[14,15] Naphthalene[34] has a rate constant $k_{ET} = 6.7 \times 10^8 \, M^{-1} s^{-1}$ and dibenzofuran[35] $2.0 \times 10^9 \, M^{-1} s^{-1}$. By comparison with these values the rate constant for 2 seems reasonable.

Only a few rate constants of self-exchange reactions between neutral aromatic compounds and their radical cations in acetonitrile have been measured. Both ex situ and in situ generation of the radical cations were used, and the EPR measurements were carried out in the slow as well as in the fast exchange limit. The published rate constants vary considerably. In acetonitrile the highest k_{ET} was found for phenothiazine[36] ($k_{ET} = 4.2 \times 10^9 \, M^{-1} s^{-1}$ or[35] $6.7 \times 10^9 \, M^{-1} s^{-1}$), its derivative 10-methylphenothiazine[35] ($k_{ET} = 2.2 \times 10^9 \, M^{-1} s^{-1}$) and the structural similar compound phenoxazine[35] ($k_{ET} = 4.5 \times 10^9 \, M^{-1} s^{-1}$). In comparison the rate constant of phenoxathiin[35] was much lower ($k_{ET} = 3.6 \times 10^8 \, M^{-1} s^{-1}$). Some p-phenylene-diamine derivatives were measured in acetonitrile by the groups of Grampp[37] and Bard.[35] Their rate constants were in the range $3.2 \times 10^8 - 1.2 \times 10^9 \, M^{-1} s^{-1}$. Furthermore the rate
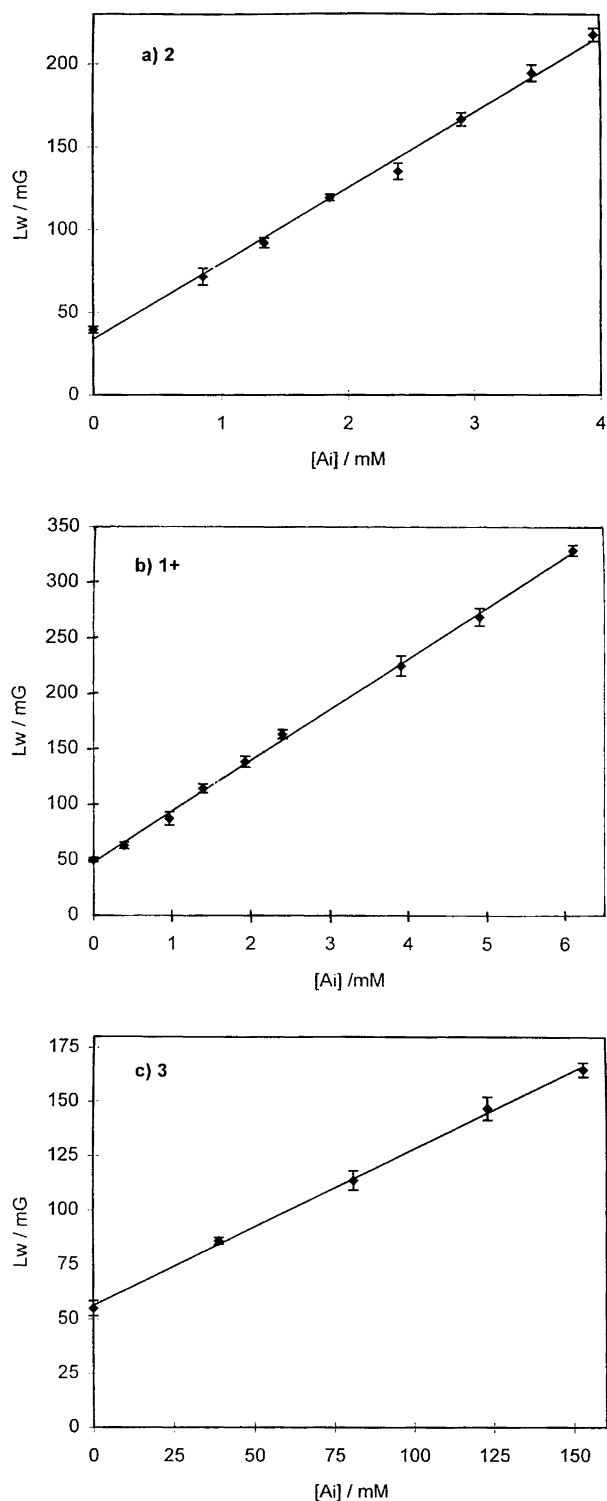
Fig. 1. Corrected EPR linewidths Lw vs. the concentration of the parent aromatic compound $[A_i]$ at low radical concentration $(2^-$ and 1, 0.1 mM; 3^{+}, 0.05 mM) for (a) $2/2^-$ (b) $1^+/1$ and (c) $3/3^{+}$. For conditions see the text.

constant of dibenzo-p-dioxine[38] was determined to be 1.5×10^9 M^{-1} s^{-1} and that of 9,10-diaminoanthracene[17] to be 2.5×10^9 M^{-1} s^{-1}. These data show that the published self-exchange rate constants of radical cations

cover a great range. The values for p-phenylenediamine derivatives are generally lower than the values for the phenothiazines. A comparison of k_{ET} and λ for $3/3^{+}$ is not possible because self-exchange ET reactions of similar compounds have not been published; its rate constant $(k_{ET} = 1.1 \times 10^7$ M^{-1} s$^{-1})$ is relatively small. The low exchange rate may be caused by the bulky $tert$-butyl groups which hinder a close approach of the π-systems.

The rate constant k_{ET} of the self-exchange reaction $1^+/1$ was determined to be 7.7×10^8 M^{-1} s^{-1} and the self-reorganization energy to be 11.3 kcal $\times$ mol^{-1} but no reasonable comparison can be made as there are only few examples of this kind of reaction in the literature.

We attempted to obtain the rate constant of the self-exchange ET from $1/1^-$ but this task proved to be the most difficult due to relatively low chemical stability of 1 and 1^- at higher concentrations. Besides monitoring the radical concentration by EPR, UV spectroscopy was used to control the concentration of the anion, 1^-. The UV–VIS spectra of 1^+, 1 and 1^- were obtained using a combination of HPLC-pump, flow cell and UV spectrometer. 1^+ absorbs at 278 nm and 1^- has a broad absorption at 310 nm. 1 shows strong absorptions at 306 and 400 and a weak one at 650 nm. In the EPR experiments 1 and 1^- were stable under the chosen conditions. The absorption of 1^- was followed in the region $480–520$ nm to ensure that its concentration remained constant during the measurements.

Experiments were conducted with different 1^- concentrations. A significant increase in linewidth of ca. 20 mG could first be detected with an anion concentration equal to 10 mM. Since it was difficult to keep the radical and the anion concentration strictly constant an increase in the uncertainty of the measured linewidth is expected. No other values could be obtained, because with a higher anion concentration a low concentration of an unknown radical was detected. The unknown radical had a complex structure and might be a coupling product or a charge-transfer complex. With the available data the rate constant can be estimated to be more than a factor ten lower than the rate constant of the reaction between 1^+ and 1. This corresponds to a λ-value higher than that of an aromatic hydrocarbon (about 10 kcal) and may explain why k_{SUB}/k_{ET} (Ref. 2) for 1^- in the reaction with sterically very hindered alkyl halides is smaller than 1.

The measurement of self-exchange reorganization energies for anionic substrates are of interest for evaluating the electron-donating capabilities of anionic nucleophiles. The approach presented here for $1/1^-$ where both species are electrogenerated from 1^+ is not easy to perform owing to the problems in controlling the concentrations of both 1 and 1^-. The problem should, however, be smaller for faster self-exchange ET reactions because smaller concentrations are necessary. Another approach is to generate the anionic species chemically, for instance by deprotonation using strong bases, and then generate the radical species by electrochemical oxidation of the anionic substrate. This approach will then be similar to

Table 1. Observed rate constants $k_{ET,obs}$, corrected rate constants k_{ET}, and reorganization energies for some self-exchange ET reactions of electrochemically generated aromatic radicals at 293 ± 1 K.

Compound	Solvent	Correlation coefficient	$k_{ET,obs}/10^8$ M^{-1} s^{-1}	$k_{ET}/10^8$ M^{-1} s^{-1}	λ/kcal mol^{-1}
3/3$^{+\cdot}$	CH$_3$CN	0.998	0.11(0.01)	0.11(0.01)	21.2(0.4)
2/2$^{-\cdot}$	DMF	0.995	6.9(0.5)	7.7(0.6)	11.3(0.3)
1$^+$/1$^\cdot$	DMF	0.999	7.0(0.5)	7.7(0.6)	11.3(0.3)

the one used for measuring 1$^+$/1$^\cdot$, i.e., oxidizing the substrate instead of reducing it. For 1$^\cdot$/1$^-$ this alternative approach is, however, not applicable because 1$^-$ could not be synthesized as a stable salt.

The present set-up was found to be a powerful device for obtaining rate constants. One advantage was a relatively simple cell construction. It was easy to handle and to clean. The flow cell was effectively producing a constant radical concentration under steady-state conditions. This allowed recording of EPR spectra of unstable radicals with a lifetime greater than 3 s. Even more unstable radicals can be measured, when a pump with a higher flow rate is used. The disadvantage of the system was high consumption of substance and solvent. This problem was partly circumvented by recording only parts of the spectra. It is an additional advantage that the combination of HPLC-pump and flow cell can easily be connected to other spectroscopic apparatus, such as a UV or IR spectrometer.

The procedure outlined here includes three important improvements compared with many previous studies. The first improvement is that the concentration of radical is repeatedly measured and assured to be constant and low. Fluctuations in radical concentration will influence the line-broadening of the EPR lines. The second improvement is that linewidths are not measured directly from the EPR spectra but are extracted from digitally simulated spectra. The precision in the linewidth is much improved by this method. The final improvement is obtained by introducing a temperature control close to the EPR cell. When the radicals are formed electrochemically some heat is produced in the electrochemical cell which might raise the temperature of the solution in the EPR cell. The same can happen when electrical valves are situated too closely to the EPR cell. Temperature fluctuation will change the k_{ET} rate constant and therefore the linewidth. Results of self-exchange ET rate constants obtained by different methods in different laboratories show fluctuations much higher than expected from the published uncertainty limits. Hopefully these new improved methods will diminish these discrepancies.

Conclusions

The rate constants for the self-exchange ET reaction between the aromatic parent compounds 3, 2 and 1$^+$ and their radicals have been determined. The measured rates have been compared with literature values for similar compounds. In this work an improved electro-

chemical flow cell system was connected to an EPR cell to measure line-broadenings. It has been demonstrated that this system and the general procedures described here give reproducible results.

Experimental

Reagents. Acetonitrile (Prolabo) and N,N-dimethylformamide (DMF) (Prolabo) were used without further purification. The supporting electrolyte tetrabutylammonium tetrafluoroborate Bu$_4$NBF$_4$ was prepared by standard methods, recrystallized from ethyl acetate and dried carefully. Before each experiment the electrolyte was dried by passage through a column of activated alumina. 2 was commercially available and 1$^+$ and 3 were prepared by standard procedures.

Instrumentation. EPR spectra were recorded at 293 ± 1 K on a Bruker ER 200 spectrometer with a modulation frequency of 25 kHz. The temperature was registered with an Advanced DPM 300 digitaltermometer. UV–VIS spectra were recorded on a Hewlett Packard 8452 spectrophotometer. An HPLC pump (Kontron Instruments Pump 420, flow: 0.05–10 ml min^{-1}) was used to obtain a constant flow.

Radical generation. For the generation of radicals a flow cell similar to the one described by Larsen et al.[14,15] was used with some modifications. The cell material of the housing was changed to the inert PCFE (KEL-F). Carbon fibers were used as working electrode and pressed tightly into a porous ceramic TZ-tube ($\phi_o = 16$ mm, $\phi_i = 5$ mm, length = 50 mm) from Export Technische Keramik, München, Germany. As a counter electrode a gold net was wound around the cylinder. The contacts to the working and the counter electrodes were made with platinum wires through the housing. The flow cell was normally used galvanostatically, however, when used potentiostatically an Ag/AgI reference electrode (also in flow-through conditions) was connected to the flow cell. It was connected closely to a flat EPR cell giving a dead volume of 0.5 ml. A constant flow rate up to 10 ml min^{-1} could be obtained with the HPLC-pump, so the dead time could be reduced to 3 s.

Procedure. All solutions (DMF or acetonitrile solvents with 0.02 M Bu$_4$NBF$_4$) were deaerated before use by bubbling nitrogen or argon through the solution for 20 min followed by ultrasonication. The flow rates were

1.3 ml min^{-1} for **1**$^+$, 1.4 ml min^{-1} for **2** and 6 ml min^{-1} for **3**. Before any measurement of self-exchange kinetics the concentration of radical had to be adjusted. Low concentrations of substrates (**2** and **1**$^+$, 0.1 mM; **3**, 0.05 mM) were employed. The current was adjusted to perform a one-electron reduction of the substrate. With a modulation amplitude of 14 G and a modulation frequency of 25 kHz the EPR spectrum collapsed to a single broad line, the intensity of which was proportional to the concentration of the electrogenerated radical.[14,15,39] The height/intensity of the strongly overmodulated EPR spectrum representing the radical concentration was measured and kept constant throughout the series of line-broadening experiments by varying the current. The high-resolution spectrum was then recorded with a modulation amplitude of 32 mG. The EPR spectrum at zero concentration of substrate was recorded and ΔB_0 could be determined by fitting to simulated spectra.

Solutions with higher concentrations of substrate were measured with the same radical concentration, controlled by the overmodulated EPR signal and adjusted by varying the electrolysis current. The deviation of radical concentration could be held to under 4%. Only parts of the high-resolution spectra were measured to make more accumulations possible and improve the signal to noise ratio.

For the reduction of **1**$^+$ to **1**$^-$ two flow cells were connected. The first flow cell was used potentiostatically to reduce **1**$^+$ to **1**$^{\cdot}$ and the second galvanostatically to reduce **1**$^{\cdot}$ to **1**$^-$. The **1**$^{\cdot}$ concentration was held at 0.1 mM. The experiments were conducted in DMF with 0.1 M Bu$_4$NBF$_4$. The concentrations of **1**$^+$, **1**$^{\cdot}$ and **1**$^-$ were monitored by UV spectroscopy. The flow-through cuvette for the UV spectrometer was situated after the EPR cell. The rest of the procedure was the same as described above.

Simulation and evaluation. Spectra were simulated digitally on a Unix Alpha computer. In the program a Lorentzian lineshape was assumed. All parameters (coupling constants, average linewidth and offset) were optimized by an iterative optimization procedure.[40]

The linewidth ΔB_i is an average value obtained from two to four experimental spectra. To improve the signal-to-noise ratio and reduce the consumption of chemicals, only part of a spectrum from a given radical was measured. Accordingly, the linewidths ΔB_i and ΔB_0 had to be corrected with the weighted normalisation factor

$$P = \sum_i (1 - p_i)/X,$$

with the summation running over lines in the selected part only (p_i = normalized population factor for line i and X = number of lines in selected part). The corrected linewidth (Lw = $\Delta B_i/P$) was plotted vs. the concentration of parent aromatic compound [A$_i$]. The slope and correlation coefficient were determined by linear least-squares analysis. The error bars give the errors obtained

through averaging and simulation, and through the uncertainty in radical concentration.

References

1. Eberson, L. *Electron Transfer Reactions in Organic Chemistry*, Springer Verlag, Berlin 1987.
2. Lund, H., Daasbjerg, K., Lund, T. and Pedersen, S. U. *Acc. Chem. Res.* **28** (1995) 313; Lund, H and Kristensen, L. *Acta Chem. Scand., Ser. B 33* (1979) 495.
3. Lund, T. and Lund, H. *Tetrahedron Lett.* **27** (1986) 95.
4. Lund, T. and Lund, H. *Acta Chem. Scand., Ser. B 40* (1986) 470.
5. Lund, T. and Lund, H. *Acta Chem. Scand., Ser. B 41* (1987) 93.
6. Daasbjerg, K., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* **43** (1989) 876.
7. Daasbjerg, K., Lund, T. and Lund, H. *Tetrahedron Lett.* **30.** (1989) 493.
8. Daasbjerg, K., Pedersen, S. U. and Lund, H. *Acta Chem. Scand.* **45** (1991) 424.
9. Szwarc, M. and Jaguar-Grozinski, J. In: Szwarc, M., Ed., *Ions and Ion Pairs in Organic Reactions*, Wiley, New York 1974, p. 1.
10. Eberson, L. *Adv. Phys. Org. Chem.* **18** (1982) 79, and references therein.
11. Harrer, W., Grampp, G. and Jaenicke, W. *Chem. Phys. Lett.* **112** (1984) 263.
12. Grampp, G. *Z. Phys. Chem. N.F.* **148** (1986) 53.
13. Grampp, G., Harrer, W and Jaenicke, W. *J. Chem. Soc., Faraday Trans. 1,* **83** (1987) 161.
14. Larsen, H. Diploma Thesis, Århus Universitet 1992.
15. Larsen, H., Pedersen, S. U., Pedersen, J. A. and Lund, H. *J. Electroanal. Chem., 331* (1992) 971.
16. Bard, A. J., Ledwidth, A. and Shine, H. J. *Adv. Phys. Org. Chem. 13* (1976) 155.
17. Grampp, G. and Jaenicke, W. *Ber. Bunsenges. Phys. Chem.* **88** (1984) 325, and references therein.
18. Fuhlendorff, R., Lund, T., Lund, H. and Pedersen, J. A. *Tetrahedron Lett.* **28** (1987) 5335.
19. Goez, M. *Z. Phys. Chem. N.F. 169* (1990) 133.
20. Jones, M. T. and Weissman, S. I. *J. Am. Chem. Soc. 84* (1962) 4269.
21. Lown, J. W. *Proc. Chem. Soc. London* (1963) 283.
22. Castellano, A., Catteau, J. P. and Lablache-Combier, A. *J. Phys. Chem. 80* (1976) 2614.
23. Kubota, S. and Ikegami, Y. *J. Phys. Chem. 82* (1978) 2739.
24. Bernal, I., Rieger, P. H. and Fraenkel, G. K. *J. Chem. Phys. 37* (1962) 1489.
25. Sullivan, P. D. and Brette, N. A. *J. Chem. Phys. 79* (1975) 474.
26. Ward, R. L. and Weissmann, S. I. *J. Am. Chem. Soc. 79* (1957) 2086.
27. Zandra, P. J. and Weissmann, S. I. *J. Chem. Phys. 35* (1961) 757.
28. Waller, A. M. and Compton, R. G. *Compr. Chem. Kinet.* **29** (1989) 297, and references therein.
29. Weast, R. C., Ed., *Handbook of Chemistry and Physics*, CRC Press, Boca Raton 1994.
30. Riddik, J. A., Bunger, W. B. and Sakano, T. *Organic Solvents, Properties and Methods of Purification*, 4th ed., Wiley Interscience, New York 1986.
31. Marcus, R. A. *J. Am. Chem. Soc. 67* (1963) 853.
32. Marcus, R. A. *J. Chem. Phys. 26* (1957) 867.
33. Ward, R. L. *J. Am. Chem. Soc. 83* (1961) 1296.

34. Sullivan, A. E. J., Peover, M. E. and Wilson, R. *Trans. Faraday Soc. 66* (1970) 1322.

35. Kowert, B. A., Marcoux, L. and Bard, A. J. *J. Am. Chem. Soc. 94* (1972) 5538.

36. Sorensen, S. P. and Bruning, W. H. *J. Am. Chem. Soc. 95* (1973) 2445.

37. Grampp, G. and Jaenicke, W. *Ber. Bunsenges. Phys. Chem. 95* (1991) 904.

38. Sorensen, S. P. and Bruning, W. H. *J. Am. Chem. Soc. 94* (1972) 6352.

39. Nozaki, K., Naito, A., Ho, T.-I., Hatano, H. and Okazaki, S. *J. Phys. Chem. 93* (1989) 8304.

40. Axelsen, V. and Pedersen, J. A. *J. Chem. Soc., Faraday Trans. 1, 83* (1987) 107.