

Solvent Effects on the Kinetics and Thermodynamics of the Reversible Dimerization of 9-Cyanoanthracene Anion Radical

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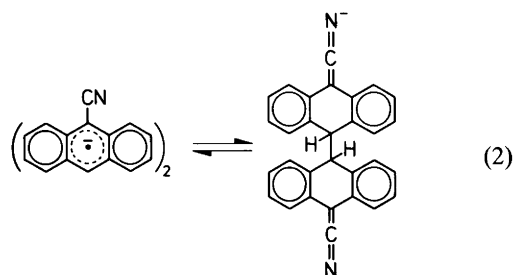
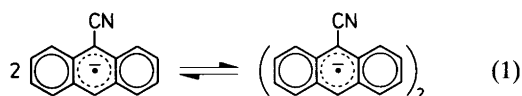
Eliason, R., Hammerich, O. and Parker, V. D., 1988. Solvent Effects on the Kinetics and Thermodynamics of the Reversible Dimerization of 9-Cyanoanthracene Anion Radical. – Acta Chem. Scand., Ser. B 42: 7–10.

The kinetic and thermodynamic parameters for the reversible dimerization of 9-cyanoanthracene (ANCN) anion radical [eqn. (i)] were determined in six



aprotic solvents. For the dissociation of the dimer, the values of $\log(k_{-i}/\text{s}^{-1})$ were observed to correlate well (correlation coefficient $r=0.97$) with the solvent acceptor numbers (AN), while a poor correlation ($r=0.82$) was observed for $\log(k_i/\text{M}^{-1}\text{s}^{-1})$. At 298 K, k_i varied by a factor of 13 and K_i by a factor of 37 as the solvent was changed, with the extreme values observed for acetonitrile (greatest values) and hexamethylphosphoric triamide. Thermodynamic parameters, ΔH_i and ΔS_i , varied within the ranges -10.5 to -14.9 kcal mol⁻¹ and -20 to -30 cal K⁻¹ mol⁻¹, respectively. Activation parameters, ΔH_i^\ddagger and ΔS_i^\ddagger , ranged from -0.5 to 4.5 kcal mol⁻¹ and -23 to -32 cal K⁻¹ mol⁻¹, respectively. The data are most consistent with a two-step mechanism involving the initial formation of a π -complex prior to bond formation.

The reversible dimerization of 9-cyanoanthracene anion radical in aprotic solvents has been studied extensively.¹⁻⁶ This process would appear to be ideal as a model system for anion radical dimerization since no side reactions have been observed and the product of the reaction, the dimer dianion, is stable in solution. Although some controversy arose in the initial mechanism studies^{3,4} regarding whether the reaction could be considered as a simple dimerization of two anion radicals^{4,6} or it is necessary to include the formation of an intermediate complex before bonding takes place,³ evidence for the two-step mechanism appears to be indisputable. The reaction mechanism can be formulated as in eqns. (1) and (2).



The reaction was originally studied in *N,N*-dimethylformamide (DMF),¹⁻³ and data for dimethyl sulfoxide (DMSO) are also available.⁴⁻⁶ The emphasis in these studies has centered around the overall rate and equilibrium con-

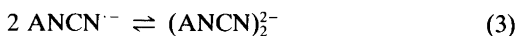
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stants, together with the activation energies for the forward reaction.

We have now completed a detailed study of the effect of temperature and solvent on the rate and equilibrium constants for the reaction.

Results and discussion

Distinguishing between a simple one-step equilibrium [eqn. (3)] and the two-step, pre-equilibrium



mechanism [eqns. (1) and (2)] is not a trivial problem. We have previously relied on activation energy arguments, i.e. that low and negative activation energies are a reflection of the masking of the positive activation energy of the rate-determining step (2) by the negative enthalpy of the pre-equilibrium (1), to distinguish between the two mechanisms.^{2,3} This approach to the problem is a generally accepted one and has been applied in a number of similar cases.⁷⁻¹³

In mechanism studies it is always desirable to support conclusions based on evidence of a particular nature with evidence derived from distinctly different sources. For this reason, it would be of great interest to develop further criteria to distinguish between these two general mechanistic possibilities. In this paper we investigate the use of rate constant-solvent parameter relationships as mechanistic criteria to distinguish between single step [eqn. (3)] and two-step [eqns. (1) and (2)] dimerization mechanisms.

A great deal of effort has been directed toward the assignment of solvent parameters which can be used to predict the effect of a change in solvent on the rate and equilibrium constants for chemical reactions in solution.¹⁴ The donor numbers (DN) and acceptor numbers (AN) described by Gutmann¹⁵ are among the most useful quantities in ion radical chemistry.¹⁶⁻²² These parameters describe the nucleophilic (DN) and the electrophilic (AN) behaviour of the solvents.

For the general cases, the mechanisms can be written as in (4) for the one-step mechanism or as (5) + (6) for the pre-equilibrium followed by rate-determining bond formation. Considering first the expected response of reaction (4) to



changes in solvent properties, reflected by the solvent parameters, it is obvious that any correlation of k_4 with a set of solvent parameters will also apply in the opposite sense to k_{-4} , i.e. the correlation plots will have opposite slopes but the quality of the correlation is expected to be the same in both directions of reaction (4).

The situation is not as straightforward for the two-step case. The observed rate constant (k_{obs}) for the forward reaction is equal to $k_6 K_5$, and no simple correlation of k_{obs} with a solvent parameter is to be expected since the contribution from k_6 may (or may not) be cancelled by that from K_5 . On the other hand, the rate constant for the reverse reaction is a microscopic one, k_{-6} , and this is expected to respond to solvent properties in a normal manner. Thus, if kinetic data are available for both the forward and reverse reactions in a dimerization, correlations of rate constants with solvent parameters can provide a means of distinguishing between the two mechanistic possibilities. If equally good correlations (of opposite slope) are observed for the forward and reverse reaction rate constants, the simple one-step mechanism is the most likely. If a poor (or no) correlation is observed for data for the forward reaction and a good correlation is observed for data for the reverse reaction, this strongly supports the assignment of a pre-equilibrium mechanism.

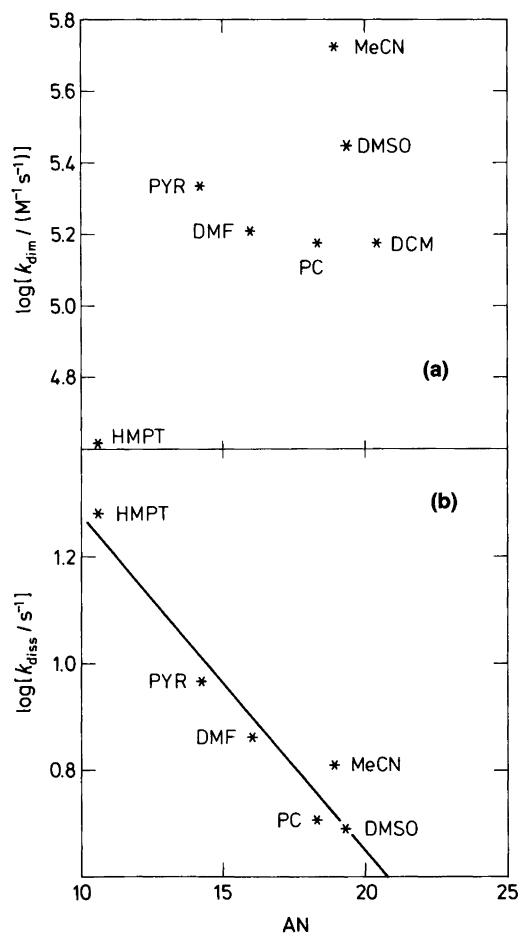
The forward rate constants and equilibrium constants for the reversible dimerization of 9-cyanoanthracene anion radical were determined in a number of aprotic solvents. The kinetic method was that described earlier²³ and is based on measurement of the minimum of the double potential step chronoamperometry response to the reversible reaction. The data are summarized in Table 1. The thermodynamic parameters are characterized by consistent values of ΔH close to $-14 \text{ kcal mol}^{-1}$ and ΔS ranging from -20 to $-30 \text{ cal K}^{-1} \text{ mol}^{-1}$. For the forward reaction, $\Delta H_{\text{dim}}^\ddagger$ is generally small and positive with one exception: it is negative for propylene carbonate as solvent, while $\Delta S_{\text{dim}}^\ddagger$ is consistently large and negative, ranging from -23 to $-32 \text{ cal K}^{-1} \text{ mol}^{-1}$. For the

Table 1. Kinetic and thermodynamic parameters for the reversible dimerization of 9-cyanoanthracene anion radical in dipolar aprotic solvents at 298 K.^a

Solvent	$10^{-4} K/M^{-1}$	ΔH	ΔS_{298}	$10^{-5} k_{\text{dim}}/M^{-1} \text{ s}^{-1}$	$\Delta H_{\text{dim}}^{\ddagger}$	$\Delta S_{\text{dim}}^{\ddagger}$	k_{diss}/s^{-1}	$\Delta H_{\text{diss}}^{\ddagger}$	$\Delta S_{\text{diss}}^{\ddagger}$
Pyridine	2.3	-13.3	-25	2.2	0.68	-32	9.3	14.0	-7
Butyronitrile	1.9	-13.1	-24	2.0	3.0	-24	10.5	16.1	0
<i>N,N</i> -Dimethylformamide	2.2	-14.5	-30	1.6	1.7	-29	7.3	16.2	1
Acetonitrile	8.2	-14.9	-28	5.3	2.2	-25	6.5	17.1	3
Propylene carbonate	2.9	-14.5	-28	1.5	-0.5	-37	5.1	14.0	-8
Hexamethylphosphoric triamide	0.22	-10.5	-20	0.41	4.5	-23	18.4	15.0	-3
Dichloromethane ^b	—	—	—	1.5	2.7	-26	—	—	—
Dimethyl sulfoxide ^c	5.7	—	—	2.8	—	—	4.9	—	—

^aIn solvent containing Bu_4NBF_4 (0.1 M). ΔH and ΔH^{\ddagger} values in kcal mol^{-1} ; ΔS_{298} and ΔS^{\ddagger} values in $\text{cal K}^{-1} \text{ mol}^{-1}$.

^bEquilibrium data could not be obtained in this solvent. ^cFrom Ref. 5.



reverse reaction, $\Delta H_{\text{diss}}^{\ddagger}$ varies very little within the range 14–17 kcal mol^{-1} , while $\Delta S_{\text{diss}}^{\ddagger}$ values are small with both positive and negative signs.

The observation of low activation enthalpies for the forward reactions in all of the solvents investigated supports our previous observations^{2,3} for the reactions in DMF, and strongly suggests that the mechanism of the reaction involves pre-equilibrium formation of a complex, followed by rate-determining bond formation to give the stable dimer dianion, as shown in eqns. (1) and (2).

An attempt to correlate k_{dim} , the observed forward rate constant, with AN by plotting $\log(k_{\text{dim}}/M^{-1} \text{ s}^{-1})$ vs. AN is shown in Fig. 1a. The correlation is very poor, as reflected by the value of the correlation coefficient, r , of only 0.69 when all the data points [except that for butyronitrile (PrCN), for which AN is not available] are used. If the data point for dichloromethane (DCM) is excluded (see below) the correlation is better, although still poor ($r = 0.82$). The analogous correlation of k_{diss} , the observed reverse rate constant, with AN is shown in Fig. 1b. In this case the correlation is good, with an r -value of -0.97 (all solvents except DCM, in which k_{diss} could not

Fig. 1. Plots of logarithms of rate constants for (a) dimerization of 9-cyanoanthracene anion radical and (b) dissociation of the dimer dianion vs. solvent AN parameters. The abbreviations refer to hexamethylphosphoric triamide (HMPT), pyridine (PYR), *N,N*-dimethylformamide (DMF), propylene carbonate (PC), acetonitrile (MeCN), dimethyl sulfoxide (DMSO) and dichloromethane (DCM).

be measured, and PrCN). The negative slope reflects a reaction involving the dimer dianion with localized charge being transformed to one or two species in which the charge is significantly more delocalized. These observations are consistent with our expectations for the pre-equilibrium mechanism.

Attempts to correlate $\log(k_{\text{dim}}/M^{-1} \text{ s}^{-1})$ and $\log(k_{\text{diss}}/\text{s}^{-1})$ with other solvent polarity parameters such as E_T ^{14,24} and Z ,^{14,25} as well as physical properties like the dipole moment, the dielectric constant and the viscosity, were in general unsuccessful. However, in one case, when Swain's "acidity" values²⁶ (A) were used, results similar to those observed for AN were obtained.

Correlations of kinetic data with empirical solvent parameters are never quantitative. Our correlation of k_{diss} with AN appears to be about as good as others reported¹⁷⁻²¹ using AN for reactions involving organic anions. It has recently been pointed out that the correlations can be improved in some cases by the inclusion of a second parameter,²² and a reasonably good correlation of electrode potentials for the formation of anion radicals with an optimally weighted function of Swain's A and B solvent polarity parameters²⁶ was observed. Our data are not extensive enough to warrant such an extended approach.

In conclusion, we regard the good correlation ($r = -0.97$) found between $\log(k_{\text{diss}}/\text{s}^{-1})$ and AN, together with the poor correlation ($r = 0.82$ for the same solvents) between $\log k_{\text{dim}}/M^{-1} \text{ s}^{-1}$ and AN as further supporting our view^{2,3} that k_{dim} does not reflect the rate of a simple bimolecular step, but rather a more complex reaction pathway including the intermediate formation of a π -complex prior to bond formation [eqns. (1) and (2)], while k_{diss} may well be associated with the simple unimolecular cleavage of the dimer dianion. The analysis presented here should be applicable to distinguish between one-step and two-step mechanisms in related cases.

Experimental

The solvents and the supporting electrolyte, Bu_4NBF_4 , were purified by standard procedures. Solvent/ Bu_4NBF_4 solutions (0.1 M) were passed through a column containing neutral alumina (Woelm W200) immediately before use. The ex-

perimental procedures, data treatment and theoretical data were as previously described.²³

References

1. Yildiz, A. and Baumgärtel, H. *Ber. Bunsenges. Phys. Chem.* 81 (1977) 1177.
2. Hammerich, O. and Parker, V. D. *Acta Chem. Scand., Ser. B* 35 (1981) 341.
3. Hammerich, O. and Parker, V. D. *Acta Chem. Scand., Ser. B* 37 (1983) 379.
4. Savéant, J. M. *Acta Chem. Scand., Ser. B* 37 (1983) 365.
5. Amatore, C., Garreau, D., Hammi, M., Pinson, J. and Savéant, J. M. *J. Electroanal. Chem.* 184 (1985) 1.
6. Amatore, C., Pinson, J. and Savéant, J. M. *J. Electroanal. Chem.* 137 (1982) 143.
7. Khudyakov, I. V., Levin, P. P. and Kuzmin, V. A. *Usp. Khim.* 49 (1980) 1990.
8. Mahoney, L. R. and DaRooge, M. A. *J. Am. Chem. Soc.* 97 (1975) 4722.
9. Caldin, E. F. and Tortschanoff, K. J. *J. Chem. Soc., Faraday Trans. 1* (1978) 1804.
10. Maharaj, U. and Winnik, M. A. *J. Am. Chem. Soc.* 103 (1981) 2328.
11. Kiselev, V. D. and Miller, J. G. *J. Am. Chem. Soc.* 97 (1975) 4036.
12. Jähme, J. and Rüdhardt, C. *Tetrahedron Lett.* 23 (1982) 4011.
13. Parker, V. D. and Tilset, M. *J. Am. Chem. Soc.* 108 (1986) 6371.
14. Reichardt, C. *Solvent Effects in Organic Chemistry*, Verlag Chemie, Weinheim 1979.
15. Gutmann, V. *Electrochim. Acta* 21 (1976) 661.
16. Opałko, M. *J. Chem. Soc., Faraday Trans. 1*, 82 (1986) 339.
17. Jaworski, J. S., Lesniewska, E. and Kalinowski, M. K. *J. Electroanal. Chem.* 105 (1979) 329.
18. Fawcett, W. R. and Jaworski, J. S. *J. Phys. Chem.* 87 (1983) 2972.
19. Santa Ana, M. A., Chadwick, I. and Gonzáles, G. *J. Chem. Soc., Perkin Trans. 2* (1985) 1755.
20. Jaworski, J. S. *Electrochim. Acta* 31 (1986) 85.
21. Kimura, N. and Takamuku, S. *Bull. Chem. Soc. Jpn.* 59 (1986) 3653.
22. Wilford, J. H. and Archer, M. D. *J. Electroanal. Chem.* 190 (1985) 271.
23. Parker, V. D. *Acta Chem. Scand., Ser. B* 37 (1983) 871.
24. Dimroth, K., Reichardt, C., Siepmann, T. and Bohlmann, F. *Liebigs Ann. Chem.* 661 (1963) 1.
25. Kosower, E. M. *J. Am. Chem. Soc.* 80 (1958) 3253.
26. Swain, C. G., Swain, M. S., Powell, A. L. and Alunni, S. *J. Am. Chem. Soc.* 105 (1983) 502.

Received July 2, 1987.