Early or Late Transition States in the Menschutkin Reaction. A Resolution of the Entropy Problem

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Summary When correctly applied, comparisons of entropies of activation with standard entropies of reaction to the product pair of dissociated ions show that transition states in Menschutkin reactions do not resemble the product dissociated ions, a conclusion that is in agreement with all previous work in terms of free energy, enthalpy, and volume.

It is now generally agreed that evidence from changes in free energy,[1-4] enthalpy,[5] and volume[1,5-7] shows that in Menschutkin and related reactions the transition state more resembles the reactants than the product pair of dissociated ions.[8] Kinetic isotope effects[9,10] and reaction field theory calculations[11] have been used to confirm the 'early' nature of the transition state. In a detailed study of reaction (1; B = pyridine and RX = MeI) using as solvent acetonitrile, Arnett and Reich[12] determined substituent effects on $\Delta G^{\ddagger}_{1}$ and $\Delta H^{\ddagger}_{1}$ and on ΔG°_{2} and ΔH°_{2} for the overall reaction (2) and showed that plots of $\delta\Delta G^{\ddagger}_{1}$ or $\delta\Delta H^{\ddagger}_{1}$ against $\delta\Delta G^{\circ}_{2}$ or $\delta\Delta H^{\circ}_{2}$ had respective slopes of 0·26 and 0·23, confirming again the early nature of the transition state.

$$\mathrm{B} + \mathrm{RX} \rightarrow \text{Product} \qquad (1)$$

$$\mathrm{B} + \mathrm{RX} \rightleftharpoons \mathrm{BR}^{+} + \mathrm{X}^{-} \qquad (2)$$

$$\mathrm{B} + \mathrm{RX} \rightleftharpoons \{\mathrm{BR}^{+}\mathrm{X}^{-}\} \qquad (3)$$

Arnett and Reich, however, also showed that for a number of substituted pyridines, $\Delta S^{\ddagger}_{1}$ was very close to ΔS°_{2}; thus for the reaction of pyridine itself with methyl iodide, $\Delta S^{\ddagger}_{1} = -30{\cdot}8$ and $\Delta S^{\circ}_{2} = -38{\cdot}4$ cal K^{-1} mol^{-1}.† On this basis, Arnett and Reich[12] concluded that in terms of entropy, the transition state resembled the product pair of dissociated ions and in order to reconcile this result with all the other evidence (above) they advanced the proposition that the transition state was 'early' with regard to the N - - $\mathrm{CH_3}$ bond formation but 'late' in terms of the $\mathrm{CH_3}$ - - I bond rupture. Kevill[13] has recently provided further evidence in terms of free energy and has suggested that the Arnett and Reich model is not correct. There is still a difficulty over the entropy result, however, and Kevill[13] has had to suggest that solvent reorganisation is more advanced than charge development in the transition state.

Table 1. The ratio $\Delta S^{\ddagger}_{1}/\Delta S^{\circ}_{2}$ for the reaction of pyridine with methyl iodide in solvent acetonitrile

Units of rate constant	$\Delta S^{\ddagger}_{1}$	ΔS°_{2}	$\Delta S^{\ddagger}_{1}/\Delta S^{\circ}_{2}$
$\mathrm{m^3\ molecule^{-1}\ s^{-1}}$	−153	−38	4·03
$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$	−31[a]	−38[a]	0·81
mole-fraction^{-1} $\mathrm{s^{-1}}$	−25	−38	0·66
$\mathrm{mm^3\ mol^{-1}\ s^{-1}}$	−3	−38	0·08
$\mu\mathrm{m^3\ mol^{-1}\ s^{-1}}$	38	−38	−1·00

[a] These are the values given by Arnett and Reich from rate constants in l $\mathrm{mol^{-1}}$ $\mathrm{s^{-1}}$; other tabulated values have been calculated from them. All $\Delta S^{\ddagger}_{1}$ and ΔS°_{2} values in cal $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ at 298 K.

We point out that whereas the numerical value of ΔS°_{2} is independent of standard states, that of $\Delta S^{\ddagger}_{1}$ depends on the units used in the calculation of the rate constant,[14,15] and therefore that the ratio $\Delta S^{\ddagger}_{1}/\Delta S^{\circ}_{2}$ also depends on these units. In Table 1 are given values of $\Delta S^{\ddagger}_{1}$ and $\Delta S^{\ddagger}_{1}/\Delta S^{\circ}_{2}$ for the reaction studied by Arnett and Reich.[12] It is clear that $\Delta S^{\ddagger}_{1}/\Delta S^{\circ}_{2}$ can take any numerical value and that from one particular value, corresponding to one particular set of concentration units, nothing can be deduced about the nature of the transition state. Although the difference $\Delta S^{\ddagger}_{1} - \Delta S^{\circ}_{3}$ is independent of standard states (unlike the

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† 1 cal = 4·184 J.

$\Delta S^{\ddagger}_{1} - \Delta S^{\circ}_{2}$ term), the ratio $\Delta S^{\ddagger}_{1}/\Delta S^{\circ}_{3}$ also depends on the units used. Similar arguments apply to ratios involving $\Delta S^{\ddagger}$ for the reverse Menschutkin reaction.

However, the variation in $\Delta S^{\ddagger}_{1}$ due to substituent effects on a reaction run in a given solvent, *i.e.* $\Delta S^{\ddagger}_{1}$ (substituent X) $-\Delta S^{\ddagger}_{1}$ (substituent Y), is quite independent of any standard state, and variations in $\Delta S^{\ddagger}_{1}$ for a given reaction run in a number of solvents depend only marginally on the chosen standard state. It is therefore reasonable to compare variations in $\Delta S^{\ddagger}_{1}$ with change of substituent or change of solvent with corresponding variations in ΔS°_{2} or ΔS°_{3}. Thus for the reaction of substituted pyridines with methyl iodide in acetonitrile,[12] we find that a plot of $\delta\Delta S^{\ddagger}_{1}$ against $\delta\Delta S^{\circ}_{2}$ has a slope of only 0·26 (*cf.* slopes of 0·26 in free energy and 0·23 in enthalpy[12]), suggesting that in terms of entropy the transition state does *not* resemble the product pair of dissociated ions. We have obtained values of $\Delta S^{\ddagger}_{1}$ and ΔS°_{2} for the Menschutkin reaction of triethylamine with ethyl iodide (Table 2). For the 7 aprotic solvents, a plot of $\delta\Delta S^{\ddagger}_{1}$ against $\delta\Delta S^{\circ}_{2}$ has a slope of 0·29, again confirming that studies using the entropy function lead to the conclusion that the transition state is 'early'.

We therefore show that the criterion used previously ($\Delta S^{\ddagger}_{1}/\Delta S^{\circ}_{2}$) to deduce the 'lateness' of the Menschutkin reaction transition state is not sound, and that when more reasonable criteria are used, such as changes in $\Delta S^{\ddagger}_{1}$ against changes in ΔS°_{2}, the results are exactly the same as those obtained using free energies, enthalpies, or volumes as the parameter investigated. All four parameters indicate that by comparison with the product pair of dissociated ions the transition state is early, with a reaction index of between *ca.* 0·2—0·3; against the product ion pair the index rises to between *ca.* 0·4—0·5, depending on the exact method of investigation. Thus the problem of the entropy of activation seems finally to have been resolved.

TABLE 2. Values of $\Delta S^{\ddagger}_{1}$ and ΔS°_{2} for the reaction of triethylamine with ethyl iodide[a]

Solvent	$\Delta S^{\ddagger}_{1}$	ΔS°_{2}
Methanol	−14	−31
Ethanol	−13	−38
Dimethyl sulphoxide	−24	−45
Dimethylformamide	−27	−59
Acetonitrile	−29	−56
Nitrobenzene	−31	−61
Acetone	−35	−66
1,2-Dichloroethane	−36	−85
1,1-Dichloroethane	−36	−85

[a] This work. All values in cal K^{-1} mol^{-1} at 298 K with $\Delta S^{\ddagger}_{1}$ calculated from rate constants in mole-fraction^{-1} s^{-1}.

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[1] M. H. Abraham, *J. Chem. Soc. B*, 1971, 299.
[2] M. H. Abraham, *J. Chem. Soc., Perkin Trans.* 2, 1972, 1343.
[3] M. H. Abraham and P. L. Grellier, *J. Chem. Soc., Perkin Trans.* 2, 1976, 1735.
[4] T. Matsui and N. Tokura, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1751.
[5] Y. Kondo, S. Hirano, and N. Tokura, *J. Chem. Soc., Perkin Trans.* 2, 1979, 1738.
[6] W. J. le Noble and T. Asano, *J. Am. Chem. Soc.*, 1975, **97**, 1778.
[7] Y. Kondo, M. Shinzawa, and N. Tokura, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 713.
[8] M. H. Abraham, *Progr. Phys. Org. Chem.*, 1974, **11**, 1.
[9] C. G. Swain and N. D. Hershey, *J. Am. Chem. Soc.*, 1972, **94**, 1901.
[10] T. M. Bare, N. D. Hershey, H. O. House, and C. G. Swain, *J. Org. Chem.*, 1972, **37**, 997.
[11] M. H. Abraham and R. J. Abraham, *J. Chem. Soc., Perkin Trans.* 2, 1975, 1677.
[12] E. M. Arnett and R. Reich, *J. Am. Chem. Soc.*, 1980, **102**, 5892.
[13] D. N. Kevill, *J. Chem. Soc., Chem. Commun.*, 1981, 421.
[14] K. J. Laidler, 'Reaction Kinetics, Vol. 1, Homogeneous Gas Reactions,' Pergamon Press, London, 1963.
[15] G. B. Skinner, 'Introduction to Chemical Kinetics,' Academic Press, New York, 1974.