

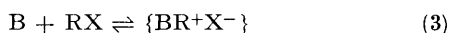
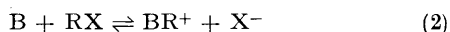
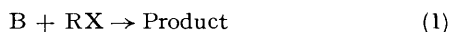
Early or Late Transition States in the Menschutkin Reaction. A Resolution of the Entropy Problem

By MICHAEL H. ABRAHAM and ASADOLLAH NASEHZADEH

(Chemistry Department, University of Surrey, Guildford, Surrey GU2 5XH)

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 calculations¹¹ 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 Reich¹² determined substituent effects on ΔG_1^\ddagger and ΔH_1^\ddagger and on ΔG_2° and ΔH_2° for the overall reaction (2) and showed that plots of $\delta\Delta G_1^\ddagger$ or $\delta\Delta H_1^\ddagger$ against $\delta\Delta G_2^\circ$ or $\delta\Delta H_2^\circ$ had respective slopes of 0.26 and 0.23, con-



firming again the early nature of the transition state. Arnett and Reich, however, also showed that for a number of substituted pyridines, ΔS_1^\ddagger was very close to ΔS_2° ; thus for the reaction of pyridine itself with methyl iodide, $\Delta S_1^\ddagger = -30.8$ and $\Delta S_2^\circ = -38.4$ cal K⁻¹ mol⁻¹.[†] On this basis, Arnett and Reich¹² 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--CH₃ bond formation but 'late' in terms of the CH₃--I bond rupture. Kevill¹³ 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 Kevill¹³ has had to suggest that solvent reorganisation is more advanced than charge development in the transition state.

We point out that whereas the numerical value of ΔS_2° is independent of standard states, that of ΔS_1^\ddagger depends on the units used in the calculation of the rate constant,^{14,15} and therefore that the ratio $\Delta S_1^\ddagger/\Delta S_2^\circ$ also depends on these units. In Table 1 are given values of ΔS_1^\ddagger and $\Delta S_1^\ddagger/\Delta S_2^\circ$ for

TABLE 1. The ratio $\Delta S_1^\ddagger/\Delta S_2^\circ$ for the reaction of pyridine with methyl iodide in solvent acetonitrile

Units of rate constant	ΔS_1^\ddagger	ΔS_2°	$\Delta S_1^\ddagger/\Delta S_2^\circ$
m ³ molecule ⁻¹ s ⁻¹	-153	-38	4.03
dm ³ mol ⁻¹ s ⁻¹	-31 ^a	-38 ^a	0.81
mole-fraction ⁻¹ s ⁻¹	-25	-38	0.66
mm ³ mol ⁻¹ s ⁻¹	-3	-38	0.08
μm ³ mol ⁻¹ s ⁻¹	38	-38	-1.00

^a These are the values given by Arnett and Reich from rate constants in l mol⁻¹ s⁻¹; other tabulated values have been calculated from them. All ΔS_1^\ddagger and ΔS_2° values in cal K⁻¹ mol⁻¹ at 298 K.

the reaction studied by Arnett and Reich.¹² It is clear that $\Delta S_1^\ddagger/\Delta S_2^\circ$ 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 $\Delta S_1^\ddagger - \Delta S_2^\circ$ is independent of standard states (unlike the

[†] 1 cal = 4.184 J.

$\Delta S_1^\ddagger - \Delta S_2^\circ$ term), the ratio $\Delta S_1^\ddagger/\Delta S_3^\circ$ also depends on the units used. Similar arguments apply to ratios involving ΔS^\ddagger for the reverse Menshutkin reaction.

However, the variation in ΔS_1^\ddagger due to substituent effects on a reaction run in a given solvent, *i.e.* ΔS_1^\ddagger (substituent X) $-\Delta S_1^\ddagger$ (substituent Y), is quite independent of any standard state, and variations in ΔS_1^\ddagger 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 ΔS_1^\ddagger 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 $\delta\Delta S_1^\ddagger$ against $\delta\Delta S_2^\circ$ has a slope of only 0.26 (*cf.* slopes of 0.26 in free energy and 0.23 in enthalpy¹²), suggesting that in terms of entropy the transition state does *not* resemble the product pair of dissociated ions. We have obtained values of ΔS_1^\ddagger and ΔS_2° for the Menshutkin reaction of triethylamine with ethyl iodide (Table 2). For the 7 aprotic solvents, a plot of $\delta\Delta S_1^\ddagger$ against $\delta\Delta S_2^\circ$ 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 ($\Delta S_1^\ddagger/\Delta S_2^\circ$) to deduce the 'lateness' of the Menshutkin reaction transition state is not sound, and that when more reasonable criteria are used, such as changes in ΔS_1^\ddagger against changes in ΔS_2° , the results are exactly the same as those

TABLE 2. Values of ΔS_1^\ddagger and ΔS_2° for the reaction of triethylamine with ethyl iodide^a

Solvent	ΔS_1^\ddagger	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 ΔS_1^\ddagger calculated from rate constants in mole-fraction⁻¹ s⁻¹.

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.

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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.