Characterization of Solute–Solvent Interaction at the Transition State by Thermodynamic and Quantum-mechanical Approaches. Reactions of Imidide Ions with Ethyl Iodide in Acetonitrile–Methanol

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Single-ion enthalpies of transfer for transition-state anions of imidide ion plus ethyl iodide reactions have been determined in acetonitrile–methanol mixtures and have been partitioned into component enthalpies, $\Delta_t H_{PHYS}^{AN\rightarrow MeOH}$ and $\Delta_t H_{SI}^{AN\rightarrow MeOH}$. Statistical analysis led to the empirical correlation incorporating nucleophiles and transition-state anions between specific interaction enthalpies, $\Delta_t H_{SI}^{AN\rightarrow MeOH}$ and the number of methanol molecules participating in the specific interaction with the anion. The molecular mechanistic origin of the specific interaction has been rationalized by introducing the concept of 'effective atomic charge on the oxygen atom' which has been derived through semi-emipirical MNDO/PM3 molecular orbital calculations.

Characterization of transition-state properties is of great importance in mechanistic organic chemistry.[1–4] The evaluation of transfer thermodynamic quantities for activated complexes on the basis of a thermodynamic cycle, *i.e.* through the combination of the activation parameters for the reaction with the transfer thermodynamic quantites for the substrates and the reactants, has been taken as the most relevant and direct experimental means for deducing transition-state properties.[5–7]

Thermodynamic properties, partly because they are the sole experimental properties usually available through standard procedures, are invoked to reflect unambiguously the molecular mechanistic properties of the initial state and the transition state. As it is possible that very many of molecular interactions are simultaneously reflected in the thermodynamic quantities, a critical examination by theoretical means is desirable for deductions made through empirical analysis to be laid on a firmer theoretical basis.

In previous work[8] the solvation patterns of imidide ions (conjugate-base anions of imides) in acetonitrile–methanol mixtures have been discussed successfully through the empirical correlation between the specific interaction enthalpies for the anions, $\Delta_t H_{SI}^{AN\rightarrow MeOH}$ and the atomic charges on the oxygen atom in the imidide ion, determined by semi-empirical, MNDO/PM3 molecular orbital calculations.

In this work, the transfer enthalpies for the transition-state anions will be determined and analysed according to the procedures developed previously,[9–12] and then the reliability of the procedures developed for the analysis of solvation patterns of imidide ions[8] will be examined by analysis of transition-state anions for the reaction of the imidide ion plus ethyl iodide in acetonitrile–methanol mixtures. Molecular interactions at the transition-state will then be discussed.

Results

Rate constants and activation parameters for five reactions of the imidide ion with ethyl iodide in acetonitrile–methanol mixtures are summarized in Table 1. There is a 200-fold variation in rate constants in acetonitrile according to structural variations in the nucleophile, and the variation of the activation enthalpy prevails over that of the activation entropy, except for reaction of 4-nitrophthalimidide. For most of these reactions the activation enthalpies in methanol exceed those in acetonitrile by *ca.* 30 kJ mol^{-1}. These features all indicate the significance of enthalpy analysis on mechanistic discussion for this type of reaction.

Single-ion enthalpies of transfer for transition-state anions (acetonitrile is taken as the reference solvent) have been calculated on the basis of a thermodynamic cycle, using the single-ion enthalpies of transfer for nucleophiles[8] and transfer enthalpies for ethyl iodide[9] and are summarized in Table 2. Those for two transition-state anions, in the reaction of 3,3-dimethylglutarimidide ion and 1-methylhydantoin anion indicate a minimum at low contents of methanol, while those for other reactions indicate a smooth variation with solvent composition. The general trend observed for transferring a transition-state anion from acetonitrile to a mixed solvent is predicted well by eqns. (1) and (2), which have also been used for the analysis of transfer enthalpies for nucleophiles.[8]

$$\Delta_t H^{AN\rightarrow mix} = \Delta_t H_{PHYS}^{AN\rightarrow MeOH} x_{MeOH}[1 - 1.23x_{MeOH}(1 - x_{MeOH})] + \Delta_t H_{SI}^{AN\rightarrow MeOH} K_{se} x_{MeOH}/(x_{AN} + K_{se} x_{MeOH}) \quad (1)$$

$$\Delta_t H^{AN\rightarrow MeOH} = \Delta_t H_{PHYS}^{AN\rightarrow MeOH} + \Delta_t H_{SI}^{AN\rightarrow MeOH} \quad (2)$$

The first term on the right-hand side of eqn. (1) generates a smooth variation of transfer enthalpies with solvent composition and serves to delineate contributions arising from the 'more physical' interactions such as ion–dipole, dipole–dipole and protophobic interactions. The second term on the right-hand side of eqn. (1) provides for a rather sharp change of transfer enthalpy in the methanol-poor region and serves to quantify 'specific' or 'more chemical' interactions such as hydrogen-bonding and dipole–dipole association interactions; K_{se} is the equilibrium constant for the solvent exchange process in the solvation site around a solute.[8–12] The calculations of enthalpies were carried out iteratively, gradually changing the parameters, $\Delta_t H_{SI}^{AN\rightarrow MeOH}$ and K_{se}, and one of the most plausible set of parameters is listed in Table 2. Transfer enthalpies for three transition-state anions, *viz.* the 3,3-dimethylglutarimidide ion, the 1-methylhydantoin anion and the 3,4,5,6-tetrachlorophthalimidide ion, were calculated using the equations with a maximum deviation of 1 kJ mol^{-1}. Those for reaction of the 4-nitrophthalimidide ion showed a more linear variation than predicted by eqns. (1) and (2) with the condition,

Table 1 Rate constants and activation parameters in acetonitrile–methanol mixtures (30 °C)

	3,3-Dimethylglutarimidide + EtI			1-Methylhydantoin anion + EtI		
x_{MeOH}[a]	$k/10^{-4}$ dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$k/10^{-4}$ dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
0	1.48×10^4	51.0	−73.6	1.05×10^3	60.6	−63.9
0.10	1.60×10^2	77.2	−24.8	21.0	83.1	−22.2
0.25	31.0	81.4	−24.6	5.03	86.8	−21.9
0.50	6.70	84.5	−27.1	1.55	89.1	−24.1
0.75	2.86	83.8	−36.5	0.685	89.9	−28.2
1.0	0.954	84.2	−44.3	0.283	92.0	−28.6

	4-Nitrophthalimidide + EtI			3-Nitrophthalimidide + EtI		
x_{MeOH}	$k/10^{-4}$ dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$k/10^{-4}$ dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
0	1.54×10^2	56.7	−92.7	1.14×10^2	63.9	−71.5
0.10	9.92	78.0	−45.2	9.65	80.4	−37.6
0.25	2.84	83.7	−36.8	2.62	84.9	−33.5
0.50	0.916	84.6	−43.3	0.879	87.5	−34.0
0.75	0.392	87.8	−39.8	0.345	98.9	−4.2
1.0	0.191	90.0	−38.5	0.188	99.7	−6.6

	3,4,5,6-Tetrachlorophthalimidide + EtI		
x_{MeOH}	$k/10^{-4}$ dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
0	61.5	66.8	−67.0
0.10	7.35	81.7	−35.5
0.25	2.41	83.9	−37.5
0.50	0.849	84.9	−42.9
0.75	0.419	87.4	−40.5
1.0	0.184	89.5	−40.5

[a] x_{MeOH} is the mole fraction of methanol.

Table 2 Single-ion enthalpies of transfer and interaction parameters for transition-state anions in acetonitrile–methanol mixtures[a]

x_{MeOH}	TS$^-$ (Me$_2$–Glutar)	TS$^-$ (Me–Hydantoin)	TS$^-$ (4-NO$_2$–Phthal)	TS$^-$ (3-NO$_2$–Phthal)	TS$^-$ (Cl$_4$–Phthal)
0	0.0	0.0	0.0	0.0	0.0
0.10	−10.5	−9.0	2.2	−1.2	0.9
0.25	−11.1	−8.5	8.1	2.1	1.9
0.50	−8.65	−4.55	10.3	5.9	3.45
0.75	−5.0	−0.4	16.45	19.9	8.7
1.0	0.7	7.3	22.65	25.3	14.2
$\Delta_t H_{PHYS}^{AN\to MeOH}$	15.2	19.8	22.65	30.3	15.7
$\Delta_t H_{SI}^{AN\to MeOH}$	−14.5	−12.5	0.0	−5.0	−1.5
K_{se}	40.0	47.0	1.0	13.0	8.0
Z	1.2	1.0	0.0	0.5	0.1

[a] Enthalpies are in kJ mol^{-1}. Me$_2$–Glutar, 3,3-dimethylglutarimidide; Me–Hydantoin, 1-methylhydantoin anion; 4-NO$_2$–Phthal, 4-nitrophthalimidide; 3-NO$_2$–Phthal, 3-nitrophthalimidide; Cl$_4$–Phthal, 3,4,5,6-tetrachlorophthalimidide.

$\Delta_t H_{SI}^{AN\to MeOH} = 0$ and $K_{se} = 1.0$, indicating that the contribution from specific interactions is insignificant at the transition state. Those for reaction of the 3-nitrophthalimidide ion indicated a negative deviation of 7.3 kJ mol^{-1} at $x_{MeOH} = 0.75$ from the value estimated by eqns. (1) and (2).

Discussion

Empirical correlations between the thermodynamic quantities of activation provide a method of deriving molecular mechanistic notions on solvation through the evaluation of the number of solvent molecules participating in a specific interaction with a solute. The number of solvent molecules, Z, is related to the specific interaction enthalpy, $\Delta_t H_{SI}^{AN\to MeOH}$ by eqn. (3),

$$\Delta_t H_{SI}^{AN\to MeOH} = Z\Delta_{se}H \qquad (3)$$

where $\Delta_{se}H$ is the enthalpy change associated with the solvent exchange process on the solvation site around an anion.[9–12] The single-ion enthalpy and entropy of transfer due to specific interactions are given by eqns. (4) and (5).[10–12]

$$\Delta_t H_{SI}^{AN\to mix} = \Delta_t H_{SI}^{AN\to MeOH} K_{se} x_{MeOH}/(x_{AN} + K_{se} x_{MeOH}) \qquad (4)$$

$$\Delta_t S_{SI}^{AN\to mix} = \left(\frac{Z\Delta_{se}H}{T}\right)\left(\frac{K_{se}x_{MeOH}}{x_{AN} + K_{se}x_{MeOH}}\right) + ZR\ln(x_{AN} + K_{se}x_{MeOH}) \qquad (5)$$

When the solvation numbers for the nucleophile and the transition-state anion are known, the solvent effects on the activation enthalpy and on the activation entropy due to the 'more physical' interactions can be calculated by eqn. (6), substituting the relevant quantities derived above into eqn. (6),

$$\delta\Delta Y_{PHYS}^{\ddagger} = \delta\Delta Y^{\ddagger} - \Delta_t Y_{SI}^{AN\to mix}(TS^-) + \Delta_t Y_{SI}^{AN\to mix}(Nu^-) \qquad (6)$$

Table 3 Specific interaction enthalpies and solvation numbers for nucleophiles and isokinetic temperatures

Nucleophiles	$\Delta_t H_{SI}^{AN\rightarrow MeOH}$/kJ mol^{-1}	$Z\,(Nu^-)$	β_{PHYS}/K
3,3-Dimethylglutarimidide	−49.0[8]	4.1	200
1-Methylhydantoin anion	−40.0[8]	3.4	210
Succinimidide	−37.0[12]	3.0[12]	355[12]
Phthalimidide	−26.0[12]	2.4[12]	406[12]
4-Nitrophthalimidide	−22.5[8]	1.2	485
3-Nitrophthalimidide	−23.0[8]	1.9	342
3,4,5,6-Tetrachlorophthalimidide	−18.5[8]	1.4	580

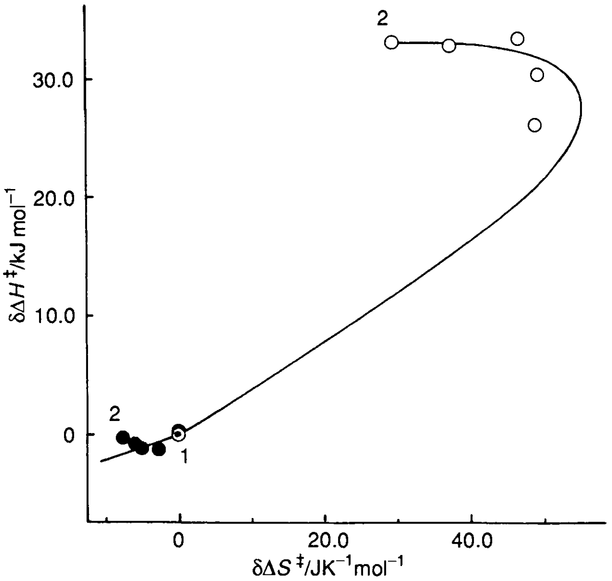


Fig. 1 Empirical correlations between activation enthalpies and activation entropies for the reaction of 3,3-dimethylglutarimidide ion with ethyl iodide in acetonitrile–methanol mixtures. ○, Overall quantities; ●, 'more physical' interaction quantities, (—) calculated quantities (see text). 1, Acetonitrile; 2, methanol.

where Y stands for enthalpy or entropy.[9–12] The required quantities for these calculations, except the solvation numbers, have already been determined, and summarized in Table 2 (for transition-state anions) and in Table 2 of ref. 8 (for nucleophiles). Calculations were repeated iteratively for assumed sets of $Z\,(Nu^-)$ and $Z\,(TS^-)$, until a linear correlation held between activation parameters due to the 'more physical' interaction, $\delta\Delta Y^{\ddagger}_{PHYS}$. The isokinetic temperature, β_{PHYS}, defined by eqn. (7), and solvation numbers for the transition-state anions and nucleophiles deduced using these treatments are summarized in Tables 2 and 3.

$$\delta\Delta H^{\ddagger}_{PHYS} = \beta_{PHYS}\delta\Delta S^{\ddagger}_{PHYS} \qquad (7)$$

Internal consistency has been tested through correlation of $\delta\Delta H^{\ddagger}_{PHYS}$ *vs.* $\delta\Delta G^{\ddagger}_{PHYS}$, which is recommended on the grounds of statistics,[13] and through the back-calculation of $\delta\Delta H^{\ddagger}$ and $\delta\Delta S^{\ddagger}$ values.[11,12] An example is shown in Fig. 1.

β_{PHYS} increases with the specific interaction enthalpy of the nucleophile, $\Delta_t H_{SI}^{AN\rightarrow MeOH}$, except for reaction of 3-nitrophthalimidide (see Table 3). The specific interaction enthalpy reflects the amount of negative charge on oxygen:[8] as the anionic charge becomes more delocalized, the hydrogen-bonding interaction between the anion and methanol is weakened,[8] and the weakening of hydrogen-bonding interaction due to the dispersion of anionic charge on going from reactants to transition state is also shown by the increase in $\Delta_t H_{SI}^{AN\rightarrow MeOH}$ (see Table 2 and Fig. 2). Solvent molecules firmly oriented around the oxygen atom in the nucleophile become partially relaxed at the transition state according to the delocalization of their anionic charge, and the extent of variation from a 'more oriented' to a 'partially relaxed' state would be diminished with increasing charge delocalization in the nucleophile. The reaction of the most charge-localized nucleophile, 3,3-dimethylglutarimidide, shows the largest variation in $\Delta_t H_{SI}^{AN\rightarrow MeOH}$, *i.e.* from −49.0 to −14.5 kJ mol^{-1}, while that of the most charge delocalized nucleophile, tetrachlorophthalimidide, shows the least variation, *i.e.* from −18.5 to −1.5 kJ mol^{-1} (see Table 2). The general trend observed between β_{PHYS} and $\Delta_t H_{SI}^{AN\rightarrow MeOH}$ for the nucleophile suggests that the differential effects of charge delocalisation on thermodynamic quantity of solvation between the initial and transition states can be sensed by β_{PHYS}; this is analogous to the observation for Menschutkin reactions.[14]

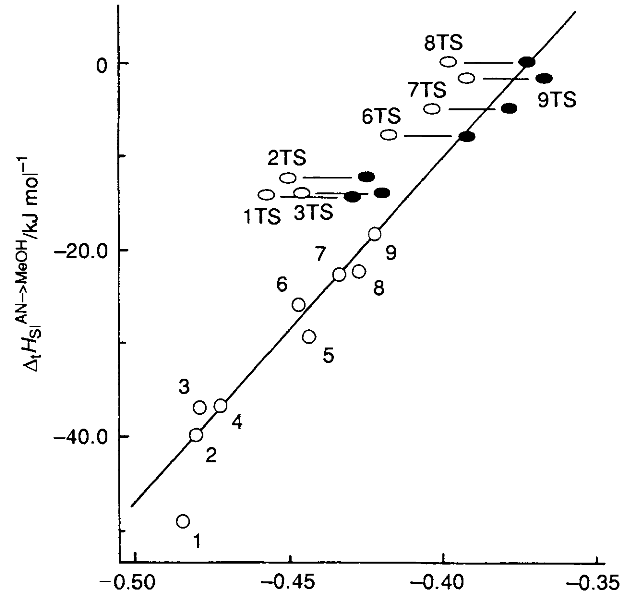
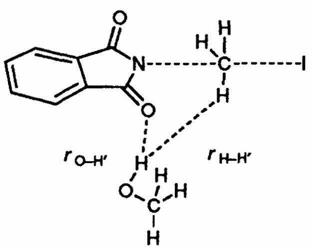


Fig. 2 Empirical correlation between specific interaction enthalpies, $\Delta_t H_{SI}^{AN\rightarrow MeOH}$ and atomic charges on oxygen. The $\Delta_t H_{SI}^{AN\rightarrow MeOH}$ values and atomic charges on oxygen for nucleophiles are from ref. 8. ○, Nucleophiles; ○, transition-state anions; ●, effective atomic charges for transition-state anions (see text). 1, 3,3-Dimethylglutarimidide ion; 2, 1-methylhydantoin anion; 3, succinimidide ion; 4, *cis*-hexahydrophthalimidide ion; 5, 2,3-napthalimidide ion; 6, phthalimidide ion; 7, 3-nitrophthalimidide ion; 8, 4-nitrophthalimidide ion; 9, tetrachlorophthalimidide ion. *i*TS, transition state anion for the reaction of ethyl iodide with the nucleophile *i*.

Statistical analysis of the enthalpy, $\Delta_t H_{SI}^{AN\rightarrow MeOH}$, *vs.* solvation number, Z, leads to eqn. (8), which holds for nucleophiles and transition-state anions ($\Delta_t H_{SI}^{AN\rightarrow MeOH}$ values for the transition-state anions in the reactions of phthalimidide and succinimidide ions are from ref. 12).



Scheme 1

$$\Delta_t H_{SI}^{AN\to MeOH} = -0.80 - 11.6{*}Z;\ n = 13, r = 0.98 \quad (8)$$

This has the physical consequence that the more basic anions are solvated by larger numbers of methanol molecules, and that the enthalpy change, $\Delta_{se}H$, or the enthalpy change of 1 : 1 interaction amounts to -11.6 kJ mol^{-1}. A similar analysis for oxygen anions and uncharged amines led to the value, $\Delta_{se}H = -13.3$ kJ mol^{-1}.[15] These analyses, together with the analysis of thermodynamic quantities of acid ionization in the aqueous phase, emphasize the significance of the 'more chemical' character of anion solvation in protic solvents.[8,9,15]

Semi-empirical molecular orbital methods provide convenient procedures for appraising the molecular and chemical properties of anions. An empirical correlation between specific interaction enthalpies, $\Delta_t H_{SI}^{AN\to MeOH}$ and the atomic charges on oxygen calculated by the MNDO/PM3 method has been found for the imidide ion series.[8] In order to examine critically the reliability of the physicochemical notions derived from the correlation, approximate saddle points for imidide ion plus methyl iodide reactions have been determined by MNDO/PM3 methods.[16] Specific interaction enthalpies for transition-state anions are plotted against atomic charges on the oxygen atom together with relevant values for imidide ions determined previously (Fig. 2). In the 4-nitrophthalimidide ion and the *N*-methylhydantoin anion the two carbonyl oxygen atoms are not equivalent. However, the differences are not significant and the average values are taken as the relevant atomic charges on oxygen either for nucleophiles or for transition-state anions. For the reaction of the 3-nitrophthalimidide ion, only the atomic charge on the oxygen that is distant from the nitro group is taken into account (see the Discussion in ref. 8). Although a moderate correlation exists between the relevant quantities for transition-state anions, the specific interaction enthalpies for transition-state anions generally deviate upwards compared with the extrapolated enthalpies from the correlation for imidide ions.

On going from the initial state to the transition state, the orientation of solvent molecules around the oxygen atom may well be affected by steric interactions with the bulk and the partial charge of the methyl group in the approaching methyl iodide. In other words, the hydrogen atoms, on the approaching methyl iodide and the hydrogen atoms in methanol bear partial positive charges, and this might bring about significant repulsive interaction into the system. An estimate of this effect can be carried out in terms of electrostatic interactions between various atomic charges in a transition-state anion and the atomic charge on the hydroxy protons in the solvating methanol. The sum of the Coulombic energy, E_C, between the atomic charge on oxygen in the nucleophile, Q_O and that on hydrogen in the solvating methanol, $Q_{H'}$, and the energy between the charge on the nearest hydrogen in the reacting methyl iodide, Q_H, and the charge on hydrogen in the solvating methanol, $Q_{H'}$, is given by eqn. (9),

$$E_C = (1/4\pi\varepsilon_0\varepsilon_r)(Q_O Q_{H'}/r_{O-H'} + Q_H Q_{H'}/r_{H-H'}) = (1/4\pi\varepsilon_0\varepsilon_r)(Q_{H'}/r_{O-H'})[Q_O + Q_H/(r_{H-H'}/r_{O-H'})] \quad (9)$$

where $r_{X-H'}$ stands for the distance between atom, X in the transition-state anion and the hydroxy hydrogen in the solvating methanol. At the initial state where the distance between nucleophile and the reacting methyl iodide can be taken as infinity, *i.e.* $r_{H-H'} \approx \infty$, the quantity in square brackets converges to Q_O, giving theoretical support for the linear correlation observed previously between specific interaction enthalpies for the nucleophile and the atomic charges on oxygen in the nucleophile.[8] The quantity in square brackets can then be taken as the 'effective atomic charge on oxygen' incorporating nucleophiles and transition-state anions. For the evaluation of $r_{O-H'}$ and $r_{H-H'}$, optimizations were carried out for four reaction systems using the configuration shown in Scheme 1 (in order to save on computation time, the N–C and C–I distances were fixed at the value determined above and the methanol was kept in the molecular plane). None of these distances varies significantly between systems, and average values, $r_{O-H'} = 4.46 \times 10^{-10}$ m and $r_{H-H'} = 1.78 \times 10^{-10}$ m are used in the following calculations. When specific interaction enthalpies for transition-state anions are plotted against 'effective atomic charges on oxygen' (Fig. 2), the nucleophiles and transition-state anions seem to fall on a single line, and a least squares analysis leads to eqn. (10).

$$\Delta_t H_{SI}^{AN\to MeOH} = 137.5 + 369.2{*}[Q_O + Q_H/(4.46/1.78)];\quad n = 16,\ r = 0.968 \quad (10)$$

The equation predicts that the specific interaction enthalpy becomes zero at an 'effective atomic charge on oxygen' of $-0.372e$. As described elsewhere,[8] $-0.372e$ is very close to the atomic charge on oxygen for uncharged *N*-methylated imides and an analysis of the tranfer enthalpies for uncharged *N*-ethylated imides did not show definitely any detectable contribution from hydrogen-bonding interactions in acetonitrile–methanol.[8] There is therefore an analogy between the prediction from the empirical correlation [eqn. (10)] and thermodynamic measurements.

Through these analyses, two types of correlations, both incorporating nucleophiles and transition-state anions and both covering a range of *ca.* 50 kJ mol^{-1}, were found empirically. The correlations and the analogy mentioned above indicate that the molecular properties at the transition state can be evaluated approximately on thermodynamic grounds, and they provide a way for bridging the gap between kinetic parameters, thermodynamic quantities and molecular properties derived through quantum-mechanical calculations.

Conclusion

Quantum-mechanical procedures have usually been used to deduce molecular mechanistic information on reactions in the gas phase. On the other hand, molecular mechanistic information on reactions in solution has had to be deduced through empirical analysis of the thermodynamic quantities which, in principle, reflect only statistically averaged characteristics of the processes concerned. The procedures of analysis presented in this work, *i.e.* the empirical correlation of thermodynamic and kinetic quantities with molecular properties derived through quantum-mechanical methods, might provide a way to examine critically the physico-chemical theories derived through more sophisticated treatments of reactions in solution.

Experimental

Materials.—Tetraalkylammonium salts containing the conjugate-base anion of imide have been prepared from tetraalkylammonium hydroxide and a relevant imide in methanol and purified as described previously.[8] Other materials were treated as described elsewhere.[10–12]

Product Analysis and Kinetic Procedures.—Stock solutions of ethyl iodide and of the relevant tetraalkylammonium imidide were mixed in a round-bottomed flask and kept overnight. After near completion of the reaction, the reaction mixtures were carefully evaporated to dryness and the solid precipitates were washed with several portions of ether several times. ^{1}H NMR spectra of the crude products (in $CDCl_3$) essentially agreed with those of the purified products [after purification by chromatography (silica-gel column) or recrystallization, the composition was confirmed by elemental analysis, as described elsewhere [8]]. Thus ethylation seems to proceed at the nitrogen atom in imidide ions as far as can be detected. Reactions were followed by measuring the iodide ion produced in the reaction by potentiometric titration using silver nitrate solution and rates were measured at four of the following temperatures, 0.0, 10.0, 20.0, 30.0, 40.0, 50.0 and 60.0 °C. Experimental errors were estimated to be *ca.* 2%, 0.5–1.0 kJ mol^{-1} and 1.7–3.0 J K^{-1} mol^{-1} for rate constants, activation enthalpies and activation entropies, respectively.

Calculations.—Semi-empirical molecular orbital calculations were carried out using the MNDO/PM3 method.[16] In order to save on computation time, the following restrictions were imposed; the framework of imidide ion has C_{2v} or C_s symmetry, methyl iodide has C_{3v} symmetry, and one of the H–C bonds in the methyl iodide approaching the imidide ion is in the plane perpendicular to the molecular plane; thus the entire reacting system retains C_s symmetry throughout. Partly because of the rather flat nature of the energy hypersurface around the saddle point, the calculated reaction coordinate for the reverse reaction was not quite the same as that of the forward reaction. Optimizations around a saddle point were carried out iteratively with the restrictions described above being imposed for *ca.* 80–100 sets of fixed N–C and C–I distances. Contour lines were drawn as a function of two independent variables, N–C and C–I distances, using the calculated enthalpies, and the saddle points were determined by visual inspection. No other refinements were carried out.

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References

1 L. P. Hammett, *Physical Organic Chemistry. Reaction Rates, Equilibria, and Mechanisms*, McGraw-Hill, New York, 2nd edn., 1970.
2 K. Mueller, *Angew. Chem.*, 1980, **92**, 1.
3 W. P. Jencks, *Chem. Rev.*, 1985, **85**, 511.
4 C. D. Ritchie, *Physical Organic Chemistry. The Fundamental Concepts*, Marcel Dekker, New York, 2nd edn., 1990.
5 E. M. Arnett, W. G. Bentrude, J. J. Burke and P. M. Duggleby, *J. Am. Chem. Soc.*, 1965, **87**, 1541.
6 A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.
7 M. H. Abraham, *Prog. Phys. Org. Chem.*, 1974, **11**, 1.
8 Y. Kondo, O. Nonaka, K. Iwasaki, T. Kuwamoto and T. Takagi, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 121.
9 Y. Kondo, M. Ittoh and S. Kusabayashi, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 2793.
10 Y. Kondo, T. Fujiwara, A. Hayashi, S. Kusabayashi and T. Takagi, *J. Chem. Soc., Perkin Trans. 2*, 1990, 741.
11 Y. Kondo, T. Hara and S. Kusabayashi, *J. Chem. Res.*, 1992, (*S*), 1, (*M*), 0101.
12 Y. Kondo, K. Kondo and S. Kusabayashi, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1141.
13 R. R. Krug, W. G. Hunter and R. A. Grieger, *J. Phys. Chem.*, 1976, **80**, 2335; 2341.
14 Y. Kondo, H. Kambe and S. Kusabayashi, *J. Chem. Soc., Perkin Trans. 2*, 1990, 915.
15 Y. Kondon, W. Sugitani and M. Tokui, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 3019.
16 MOPAC ver.6.00, J. J. P. Stewart, *QCPE Bull.*, 1989, **9**, 10.

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