Single-ion enthalpies of transfer as a scale of nucleophilic reactivity towards ethyl iodide in acetonitrile

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Logarithmic rates for nucleophilic substitution towards ethyl iodide in acetonitrile correlate well with the specific interaction enthalpies for the relevant nucleophile, $\Delta H_{t,SI}^{AN\to MeOH}$ (Nu$^-$). According to the correlation, the bromide ion reaction falls into the imidide ion reaction series, while the chloride ion reaction falls into the carboxylate ion reaction series. The partial desolvation accompanying activation is crucial in determining the reactivity behaviour of the nucleophile anions. Semi-empirical quantum mechanical calculations (MNDO/PM3 and MNDO/PM3/COSMO) give reasonable estimates for the enthalpies of activation as well as for reaction enthalpies in acetonitrile. The relative location of the transition state, estimated on the basis of empirical analysis, is in accord with the variation of electronic charges for the exposed atoms, which has been evaluated through semi-empirical quantum mechanical procedures.

The quantitative assessment of nucleophilic reactivity has long been one of the greatest concerns of physical organic chemistry, and various scales have been documented.[1-5] Since the pioneering work by Parker,[6] the significance of protic *vs.* dipolar aprotic solvent effects on organic reactions, in which an anion plays a key role, has generally been recognized.[7] Brønsted relations which make use of the relevant thermodynamic quantities determined in the dipolar aprotic solvent dimethyl sulfoxide gave credence to the linearity of the correlations, although some curved plots for data in the aqueous phase could lead to possibly unsound concepts in mechanistic organic chemistry.[8,9]

The theoretical analysis of activation parameters for aliphatic nucleophilic substitution reactions, which have been determined in acetonitrile–methanol mixtures, combined with the measurements of single-ion enthalpies of transfer for relevant nucleophiles in the same solvent mixtures, have successfully delineated the molecular mechanistic features of solute–solvent interaction at the transition state.[10-13]

In addition, the role of specific interaction enthalpy for an anion, X$^-$, $\Delta H_{t,SI}^{AN\to MeOH}$ (X$^-$), not only as a scale of hydrogen-bonding solvation in protic solvents, but also as a scale of nucleophilic reactivity for an anion, has been suggested and observed.[14,15] In the present work, in order for the significance of the enthalpy as a scale of nucleophilic reactivity to be critically examined, rate constants and activation parameters for two series of nucleophilic substitution reactions towards ethyl iodide, $Nu^- + EtI \longrightarrow Nu\text{–}Et + I^-$ (Nu$^-$; carboxylate ions and imidide ions), were measured in acetonitrile. Single ion enthalpies of transfer for the relevant nucleophiles, which have been determined in acetonitrile–methanol mixtures, were partitioned into components and empirical correlations between these quantities were analysed. Chemical interpretations, empirically derived through these procedures, are tested through semi-empirical molecular orbital calculations.

Results

Rate constants and activation parameters determined in this work for two series of nucleophilic substitution reactions, *i.e.* carboxylate ion plus ethyl iodide and imidide ion plus ethyl iodide, are summarized in Table 1. Enthalpies of solution for tetramethylammonium salts containing the relevant anion are summarized in Table 2. Single ion enthalpies of transfer have been calculated on the basis of the tetrabutylammonium/tetrabutyl borate assumption[10-13] and are summarized in Table 3.

All these thermodynamic values are characterized by a sharp decrease at a small content of methanol, followed by rather more moderate change over the region of higher content of methanol, as previously observed.[10-13] These values can be partitioned into component terms according to eqns. (1) and (2).[10-13]

$$\Delta H_t^{AN\to mix} = \Delta H_{t,PHYS}^{AN\to MeOH}\, x_{MeOH}\,[1 - 1.23\, x_{MeOH}\,(1 - x_{MeOH})] + \Delta H_{t,SI}^{AN\to MeOH}\, K_{se}\, x_{MeOH}/(x_{AN} + K_{se}\, x_{MeOH}) \quad (1)$$

$$\Delta H_t^{AN\to MeOH} = \Delta H_{t,PHYS}^{AN\to MeOH} + \Delta H_{t,SI}^{AN\to MeOH} \quad (2)$$

In eqns. (1) and (2) $\Delta H_{t,PHYS}^{AN\to MeOH}$ and $\Delta H_{t,SI}^{AN\to MeOH}$ represent the single ion enthalpy of transfer from acetonitrile to methanol arising from a 'more physical' interaction and that due to specific interaction, respectively. K_{se} stands for the equilibrium constant of the solvent-exchange process at the solvation site around a solute; x_{AN} and x_{MeOH} denote the mole fraction of acetonitrile and of methanol.[10-13]

The first term of the right hand side of eqn. (1) expresses the moderate change of transfer enthalpy with solvent composition, and is likely to contain the contributions from 'more physical' interactions such as cavity term, protophobic interaction, ion–dipole interaction, and dipole–dipole interaction, *etc.*[10-13] The second term expresses the steep changes in transfer enthalpies over the region of low content of methanol and contains contributions from such specific and 'more chemical' interactions as hydrogen-bonding, charge-transfer and dipole–dipole association interactions.[10-13]

The calculation of the enthalpies, $\Delta H_t^{AN\to mix}$, were carried out step-by-step, systematically changing the parameters K_{se} and $\Delta H_{t,SI}^{AN\to MeOH}$ until the optimum fit of the calculated values to the experimental ones was reached. The enthalpies have been simulated by the equations usually with a maximum deviation, ± 1 kJ mol^{-1}. The parameters derived are given in Table 3.

Statistical analysis of the logarithmic rate with respect to the specific interaction enthalpy leads to eqns. (3) and (4), and comparisons of the experimental values with the regression lines are shown in Fig. 1. (Enthalpies are all in kJ mol^{-1}.)

Table 1 Rate constants and activation parameters in acetonitrile (30.0 °C)

	Nucleophile				
	4-Biphenylacetate	2-Chlorophenylacetate	Phenoxyacetate	3-Nitrobenzoate	3,4-Dinitrobenzoate
$k/10^{-2}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$	10.2	6.86	2.09	1.08	0.296
$\Delta H^{\ddagger}/\mathrm{kJ\ mol^{-1}}$	62.5	61.6	66.8	67.4	68.4
$\Delta S^{\ddagger}/\mathrm{J\ K^{-1}\ mol^{-1}}$	−57.9	−64.1	−56.8	−60.4	−67.8

	Nucleophile			
	3,5-Dinitrobenzoate	*cis*-Hexahydrophthalimidide	*cis*-1,2,3,6-Tetrahydrophthalimidide	2,3-Naphthalimidide
$k/10^{-2}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$	0.290	28.2	21.1	5.74
$\Delta H^{\ddagger}/\mathrm{kJ\ mol^{-1}}$	68.8	56.6	62.0	61.4
$\Delta S^{\ddagger}/\mathrm{J\ K^{-1}\ mol^{-1}}$	−66.7	−68.9	−53.5	−66.3

Table 2 Enthalpies of solution/kJ mol^{-1} in acetonitrile–methanol mixtures (25.0 °C)

x_{MeOH}	TMA 4-biphenylacetate	TMA 2-chlorophenylacetate	TMA phenoxyacetate	TMA *cis*-1,2,3,6-tetrahydrophthalimidide
0.0	15.2	26.5	19.2	20.9
0.1	−18.1	−6.14	−10.2	−7.34
0.25	−21.0	−8.78	−12.7	−10.4
0.50	−18.3	−6.56	−10.0	−8.11
0.75	−14.5	−3.13	−6.15	−3.78
1.0	−7.89	3.09	0.658	4.23

Table 3 Single ion enthalpies of transfer[a] from acetonitrile to acetonitrile–methanol mixtures and interaction parameters (25.0 °C)

x_{MeOH}	4-Biphenylacetate	2-Chlorophenylacetate	Phenoxyacetate	*cis*-1,2,3,6-Tetetrahydrophthalimidide
0.0	0.0	0.0	0.0	0.0
0.1	−32.4	−31.7	−28.5	−27.3
0.25	−34.9	−34.0	−30.6	−30.0
0.50	−33.15	−32.75	−28.85	−28.7
0.75	−30.0	−29.9	−25.65	−25.0
1.0	−25.8	−26.1	−21.2	−19.4
$\Delta H_{\mathrm{t,PHYS}}^{\mathrm{AN\rightarrow MeOH}}$	12.2	10.9	12.8	15.6
$\Delta H_{\mathrm{t,SI}}^{\mathrm{AN\rightarrow MeOH}}$	−38.0	−37.0	−34.0	−35.0
K_{se}	70.0	70.0	65.0	42.0

[a] Enthalpies are in kJ mol^{-1}.

For carboxylate ion reactions,

$$3 + \log k = -1.53 - 8.76 \times 10^{-2} \times \Delta H_{\mathrm{t,SI}}^{\mathrm{AN\rightarrow MeOH}} \qquad (3)$$
$$n = 13, r = -0.97$$

For imidide ion reactions,

$$3 + \log k = -0.42 - 7.23 \times 10^{-2} \times \Delta H_{\mathrm{t,SI}}^{\mathrm{AN\rightarrow MeOH}} \qquad (4)$$
$$n = 10, r = -0.95$$

For either series of reactions, aliphatic nucleophiles indicate a higher reactivity in acetonitrile as well as a more favourable enthalpy of transfer from acetonitrile to methanol by comparison with aromatic nucleophiles. Carboxylate ion reactions indicate a higher sensitivity to the enthalpy change and a lower reactivity when compared at the same specific interaction enthalpy, by comparison with imidide ion reactions [Fig. 1 and eqns. (3) and (4)].

Subtle structural effects on activation enthalpy makes it difficult for the general trends to be understood through visual inspection. Statistical analysis of activation enthalpies with respect to specific interaction enthalpy leads to eqns. (5) and (6), and the comparison of the experimental values with the regression lines are shown in Fig. 2.

For carboxylate ion reactions,

$$\Delta H^{\ddagger} = 78.6 + 0.399 \times \Delta H_{\mathrm{t,SI}}^{\mathrm{AN\rightarrow MeOH}} \qquad (5)$$
$$n = 13, r = 0.86$$

For imidide ion reactions,

$$\Delta H^{\ddagger} = 71.1 + 0.349 \times \Delta H_{\mathrm{t,SI}}^{\mathrm{AN\rightarrow MeOH}} \qquad (6)$$
$$n = 10, r = 0.74$$

Lower activation enthalpies (accordingly higher reactivity) for aliphatic–nucleophile reactions in comparison to those for aromatic–nucleophile reactions either for carboxylate and imidide ion reactions, and larger activation enthalpies (accordingly lower reactivity) for carboxylate ion reactions by comparison with imidide ion reactions [Fig. 2 and eqns. (5) and (6)] can be deduced from the correlations; the trends are essentially in agreement with the trends deduced from the correlations, log *k* *vs.* $\Delta H_{\mathrm{t,SI}}^{\mathrm{AN\rightarrow MeOH}}$ as described above.

Discussion

Carboxylate ion reactions and imidide ion reactions cover comparable ranges in rate constants, activation enthalpies and the specific interaction enthalpies of nucleophiles. However, fairly large differences in the basicity have been noticed between the two series, when pK_a values of the conjugate acid in the aqueous phase have been taken as reference.[15] Bromide and chloride ions, which are often termed 'orphan nucleophiles', partly because their appropriate characterization presents difficulties through conventionally adopted scales, fall in the imidide ion series and carboxylate ion series, respectively, in terms of logarithmic rates (Fig. 1). These observations suggest that the specific interaction enthalpy serves as the relevant scale

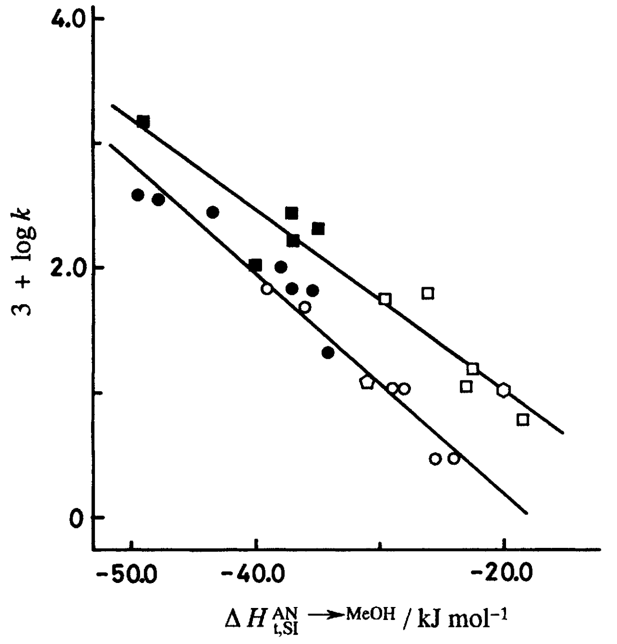


Fig. 1 Empirical correlations between the logarithmic rates for the reaction in acetonitrile (30.0 °C), $\mathrm{Nu^-} + \mathrm{EtI} \longrightarrow \mathrm{Nu{-}Et} + \mathrm{I^-}$ and the specific interaction enthalpies for relevant nucleophile, $\Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}}$ ($\mathrm{Nu^-}$).

●, aliphatic carboxylate ions; ○, aromatic carboxylate ions; ■, aliphatic imidide ions; □, aromatic imidide ions; ⬡, bromide ion; ⬠, chloride ion. Experimental results have been taken from Tables 1 and 3, and refs. 10–17.

Carboxylate ions are (in the order of increasing $\Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}}$) adamantane-1-carboxylate, diethylacetate, pivalate, 4-methoxybenzoate, 4-biphenylacetate, 2-chlorophenylacetate, benzoate, diphenylacetate, phenoxyacetate, 3-nitrobenzoate, 4-nitrobenzoate, 3,5-dinitrobenzoate and 3,4-dinitrobenzoate ions. Imidide ions are (in the order of in-creasing $\Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}}$) 3,3-dimethylglutarimidide, *N*-methylhydantoin anion, *cis*-hexahydrophthalimidide, succinimidide, *cis*-1,2,3,6-tetrahydrophthalimidide, 2,3-naphthalimidide, phthalimidide, 3-nitrophthalimidide, 4-nitrophthalimidide and 3,4,5,6-tetrachlorophthalimidide ion.

of nucleophilic reactivity in acetonitrile, and that partial bond formation at the transition state between nucleophilic and electrophilic centres is mimicked by the hydrogen-bond acceptor basicity of nucleophile, $\Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}}$.

In such weakly acidic solvents as acetonitrile ($\alpha = 0.19$[18]), the enthalpy can also be regarded as the relevant scale of nucleophile–solvent interaction. On going from initial to transition state, nucleophile anions lose part of their hydrogen-bond accepting basicity.[10–13] The increased sensitivity of logarithmic rates for different nucleophiles in carboxylate ion reactions suggests that at the transition state carboxylate ion moieties have lost to a greater extent their solvation stabilization, owing to the weakened hydrogen-bond acceptor basicity, by comparison with imidide ion moieties. In other words, the transition state for carboxylate ion reaction is located later along the reaction coordinate.

Anionic charge is mainly located on two oxygen atoms for carboxylate ions, and on three atoms, *i.e.* two oxygen atoms and one nitrogen atom, for imidide ions.[13] The extent of destabilization of the reacting system arising from decreasing anion–solvent interaction accompanying activation would be more significant for the more localized charge in carboxylate ion reactions than those for imidide ion reactions in which the anionic charge is more delocalized. This would be manifested by lower rates and larger activation enthalpies for carboxylate ion reactions, when compared at common specific interaction enthalpies.

The lower level of regression for activation enthalpy *vs.* specific interaction enthalpy correlations in comparison with those for logarithmic rate correlations indicates the intervention

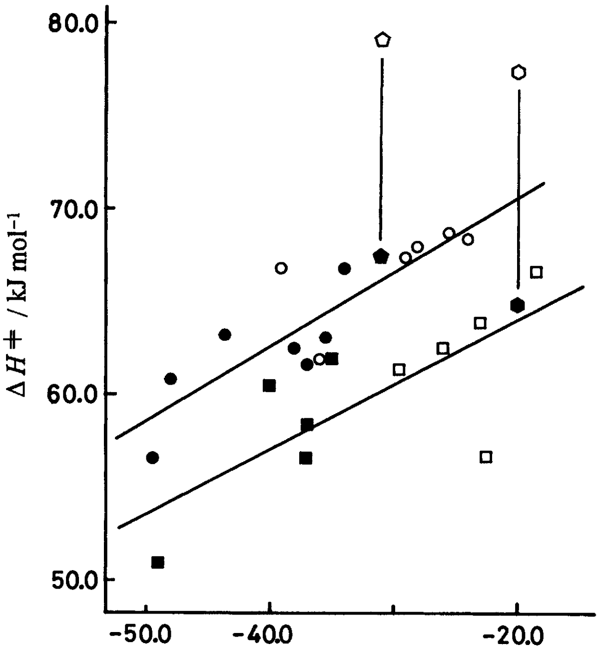


Fig. 2 Empirical correlations between the activation enthalpies for the reaction in acetonitrile (30.0 °C), $\mathrm{Nu^-} + \mathrm{EtI} \longrightarrow \mathrm{Nu{-}Et} + \mathrm{I^-}$ and the specific interaction enthalpies for relevant nucleophile, $\Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}}$ ($\mathrm{Nu^-}$).

⬢, corrected activation enthalpy for bromide ion reaction; ⬟, corrected activation enthalpy for chloride ion reaction. For other symbols, references and anions refer to Fig. 1.

of solvation enthalpy *vs.* solvation entropy compensation in these reactions. Activation enthalpies for bromide ion and chloride ion reactions indicate upward deviations from the regression lines (Fig. 2). Larger activation entropies for bromide and chloride ion reactions, −27.2 and −20.6 J K^{-1} mol^{-1},[10,11] by comparison with average activation entropies for imidide ion and carboxylate ion reactions, −68.6 and −59.3 J K^{-1} mol^{-1}, suggest a higher extent of desolvation at the transition state for the former reactions. This leads us to suppose that when the extent of partial desolvation for bromide ion reaction is the same for imidide ion reactions and that for the chloride ion reaction is the same for carboxylate ion reactions, the effects on activation enthlapies would lead to a reduction in activation enthalpy by 12.5 kJ mol^{-1} $\{= 303.15 \times [-68.6 - (-27.2)] \times 10^{-3}\}$ and 11.7 kJ mol^{-1} $\{= 303.15 \times [-59.3 - (-20.6)] \times 10^{-3}\}$ for bromide ion and chloride ion reactions. When activation enthalpies are reduced by the amount calculated above, bromide ion and chloride ion reactions again fall in with the behaviour for imidide ion and carboxylate ion families (Fig. 2).

In order to examine the credibility of the above empirically-derived notions semi-empirical molecular orbital calculations (MNDO/PM3 and MNDO/PM3/COSMO[19]) have been carried out. The relevant results are summarized in Table 4.

In the gas phase the enthalpy profile is essentially a double minimum type, with minima at ion–dipole complexes located at either side of the activated complex (transition state) as usually documented.[21] In acetonitrile, the enthalpy profile becomes a bell shape with a single maximum at a saddle point. Complex formation of benzoate ion with methyl iodide is exceptionally exothermic but the minimum is much shallower by comparison to the gas phase; essentially the same conclusion has been deduced by other means.[22]

The order of solvation stabilization evaluated through COSMO calculation is benzoate ion ~ succinimidide ion > iodide ion > transition state anion (TS$^-$) for benzoate ion reaction > TS$^-$ for succinimidide ion reaction (see Table 4)

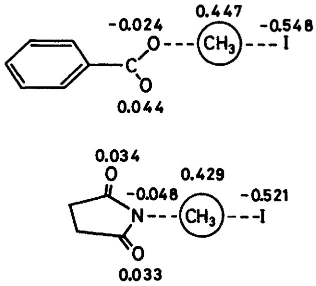
Table 4 Enthalpies of formation, activation and reaction enthalpies/kJ mol^{-1}

Benzoate + methyl iodide reaction	ΔH_f							$\Delta H^‡$ and ΔH°			
	Nu^-	CH_3I	$Nu^-\cdot CH_3I$	TS^-	$Nu\text{–}Me\cdot I^-$	Nu–Me	I^-	$\Delta H^‡_{calc}$	ΔH°_{calc}	$\Delta H^‡_{exp}$	ΔH°_{exp}
Gas	−375.8	39.5	−378.8	−341.1	−527.2	−243.5	−270.4 (−188[a])	−4.8	−177.6 (−95.2[b])	—	—
Aceto-nitrile	−749.3	27.9	−734.5	−651.5	−860.5	−290.8	−598.3 (−515.9[b])	69.9	−167.7 (−85.3[b])	61.9[c]	−74.2[c]
ΔH_{solv}	−373.5	−11.6	−355.7	−310.4	−333.3	−47.3	−327.9				
Succinimidide + methyl iodide reaction	ΔH_f							$\Delta H^‡$ and ΔH°			
	Nu^-	CH_3I	$Nu^-\cdot CH_3I$	TS^-	$Nu\text{–}Me\cdot I^-$	Nu–Me	I^-	$\Delta H^‡_{calc}$	ΔH°_{calc}	$\Delta H^‡_{exp}$	ΔH°_{exp}
Gas	−480.0	39.5	−471.7	−444.4	−657.3	−369.5	−270.4 (−188[a])	−3.9	−199.4 (−117.0[b])	—	—
Aceto-nitrile	−848.7	27.9	−821.3	−729.8	−1006.	−437.1	−598.3 (−515.9[b])	91.0	−214.6 (−132.2[b])	58.4[c]	−138.3[c]
ΔH_{solv}	−368.7	−11.6	−349.6	−285.4	−348.7	−67.6	−327.9				

[a] Experimental result, ref. 20. [b] Corrected by using the experimental enthalpy of formation for iodide ion in the gas phase. [c] Result for the reaction, $EtI + Nu^- \longrightarrow Nu\text{–}Et + I^-$, ref. 15.

Table 5 Solvents for recrystallization and elementary analysis

		Obs. (%)				Calc. (%)		
	Solvents	C	H	N	Formula	C	H	N
Tetramethylammonium 4-biphenylacetate	Acetonitrile–butan-2-one	75.9	8.08	4.95	$C_{18}H_{23}NO_2$	75.8	8.12	4.91
Tetramethylammonium 2-chlorophenylacetate	Acetonitrile–propan-2-ol	59.3	7.28	5.81	$C_{12}H_{18}NO_2Cl$	59.1	7.44	5.75
Tetramethylammonium phenoxyacetate	Acetonitrile–acetone	64.1	8.32	6.26	$C_{12}H_{19}NO_3$	64.0	8.50	6.22
Tetramethylammonium *cis*-1,2,3,6-tetrahydrophthalimidide	Acetonitrile	64.65	9.16	12.8	$C_{12}H_{20}N_2O_2$	64.3	8.99	12.5



ΔQ = atomic charge in TS anion − atomic charge in reactants

and this essentially agrees with the order of stabilization by specific interaction, *i.e.* succinimidide ion (−37.0[15]) ~ benzoate ion (−36.0[16]) > iodide ion (−20.0[10]) > TS^- for succinimidide ion reaction (−14.0[15]) > TS^- for benzoate ion reaction (−9.0[17]). The lower extent of solvation stabilization for a charge-dispersed transition state anion by comparison to a more charge-localized nucleophile anion and iodide ion is along the line of empirical expectation.[6,23]

The calculated activation enthalpy for the benzoate ion reaction in acetonitrile is comparable to the experimental result, but a somewhat larger calculated value than the experimental value is found for the succinimidide ion reaction. The calculated overall reaction enthalpies are substantially more negative compared to the experimental values. The essential deficiency of the method has often been suggested to lie in the evaluation of the enthalpy of formation for monoatomic ions. If the calculated enthalpy of formation for iodide ion is replaced by the experimental value, −188 kJ mol^{-1},[20] then the calculated reaction enthalpies are shifted towards the positive direction by the difference, 82.4 [= −188 − (−270.4)] (in kJ mol^{-1}). The corrected values (shown in parentheses) are then in accord with the experimental values.

One of the more feasible ways by which to assess the amount of solvation change accompanying activation, from a molecular mechanistic view point, would be to monitor the variation of electronic charge on the exposed atom upon which the electronic charge is supposed to indicate a monotonous change along a reaction coordinate. The variation of atomic charge accompanying activation, as defined by atomic charge in the transition-state anion minus the relevant atomic charge in the nucleophile or in methyl iodide ΔQ, has been calculated using molecular orbital results in the gas phase, and is shown in the scheme (reacting methyl group is treated as a united atom). The charge variations on the iodine atom and on the non-reacting oxygen atom are larger for the benzoate ion reaction by comparison with the succinimidide ion reaction. This indicates the transition state for the carboxylate ion reaction is located later than that for the imidide ion reaction. The results are in accord with the view as derived through the empirical considerations discussed above.

Conclusions

The specific interaction enthalpy for an anion, X^-, $\Delta H_{t,SI}^{AN\rightarrow MeOH}(X^-)$ serves as a scale of nucleophilic reactivity for the anion. The partial desolvation accompanying activation is crucial in determining the reactivity behaviour of nucleophile anions. The relative location of the transition state along the reaction coordinate, derived through empirical correlations with a specific interaction enthalpy, is in agreement with the results of semi-empirical molecular orbital calculations. Activation and reaction enthalpies in acetonitrile solvent, evaluated through the relevant theoretical procedures, are of acceptable value. However, experimental thermodynamic measurements on the relevant system are still indispensable for a sound understanding of the chemical process in solution.

Experimental

Materials

Tetramethylammonium salts containing the conjugate base anion of carboxylic acids and imides were prepared from tetramethylammonium hydroxide and the relevant carboxylic acids and imides in methanol according to essentially the same procedures as described elsewhere.[24] The salts were recrystallized three times from the solvent indicated in Table 5 and dried over phosphorus pentaoxide. The results of elementary analysis are summarized in Table 5. Other materials were treated as described elsewhere.[10–13]

Product analysis and kinetic measurements

Product analysis has been carried out according to the same procedures as described elsewhere [12,13] and ^{1}H NMR spectra of both crude and purified products agreed with those of authentic compounds.

Aliquots (5 cm^3) from stock solutions of ethyl iodide and of the relevant tetramethylammonium salts were mixed in tightly stoppered glass test tubes and the mixtures were kept in a thermostatted bath. After a given period, the reaction mixture was poured into a hexane–water mixture. The amount of iodide ion formed was determined by potentiometric titration using silver nitrate solution. The rate measurements were carried out at four of the following temperatures, 0.0, 10.0, 20.0, 30.0, 40.0 and 50.0 °C. The experimental errors were estimated to be *ca.* 2% for rate constants, *ca.* 1 kJ mol^{-1} for activation enthalpies, and *ca.* 3 J K^{-1} mol^{-1} for activation entropies.

Heat of solution measurements

Heats of solution were measured at 25.0 ± 0.1 °C with a Tokyo Riko twin isoperibol calorimeter.[10–13] Final concentration ranges of solutes were $0.4 \times 10^{-2} - 2.6 \times 10^{-2}$ dm^3 mol^{-1} and experimental errors were *ca.* 0.7 kJ mol^{-1}.

Calculations

Semi-empirical molecular orbital calculations were carried out using the MNDO/PM3 and MNDO/PM3/COSMO methods with all parameters kept as the default values.[19] In order to shorten computation time methyl iodide was used instead of ethyl iodide which has been used throughout the experiments. In the gas phase several encounter complexes of different geometry were sometimes detected. For benzoate ion complex with methyl iodide, the complex of the lowest energy was cited in Table 4. For iodide ion complex with uncharged reaction product, the complexes of analogous C–I distance, *ca.* 3.9×10^{-10} m were cited in Table 4.

Acknowledgements

We thank Dr. M. H. Abraham, University College, London for his critical reading of the original version of this manuscript and for helpful discussion, and Mr. W. Sugitani, Mr. T. Kuwamoto and Mr. M. Tokui, Osaka University for valuable technical assistance.

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Paper 6/00244G
Received 11*th January* 1996
Accepted 1*st April* 1996