Nucleophilic Reactivity and Solvation of Succinimide and Phthalimide Anions in Acetonitrile–Methanol Mixtures

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Nucleophilic reactivity and solvation patterns for succinimidide and phthalimidide ions have been characterized through three procedures, kinetic and enthalpy of solution measurements in acetonitrile–methanol mixtures, and enthalpy of reaction measurements in acetonitrile. Quantitative analysis indicates that activation enthalpy *vs.* activation entropy correlation is more sensitive and versatile than activation enthalpy *vs.* reaction ethalpy correlation as the method for detecting the effects of various molecular interactions on rates of reaction. Any essential difference in nucleophilic reactivities and in solvation patterns was not observed between imidide and carboxylate ions, but a significant difference is found on the pK_a values in the aqueous phase and on the enthalpy of reaction with ethyl iodide in acetonitrile.

The nitrogen anions are well-documented as the reagents of the first step for Gabriel synthesis of primary amines from alkyl halides.[1,2] Despite the importance of these reagents, characterization of reactivity patterns appears to have been limited, partly because of the low acidity of most N–H bonds which impedes generation of sufficient concentration of nitrogen anions in the aqeuous phase.[3,4] The recent use of dipolar aprotic solvent, DMSO as reaction media, in conjunction with the determination of acidity constants as well as rate constants in the same solvent enabled a quantitative characterization of the reactivity patterns for these anions in terms of empirical energy correlations, *i.e.*, Brönsted correlations, to be made.[5,6]

On the other hand, the combination of kinetic and enthalpy of solution measurements in acetonitrile–methanol mixtures which have been carried out for oxygen anions (carboxylate and phenolate anions) plus ethyl iodide reactions, led to the quantitative characterization of the solvation as well as the reactivity patterns for these anions and also suggested the limitation of the use of aqueous pK_a values as the reactivity index for these anions.[7,8]

In this work, kinetic and enthalpy of solution measurements have been carried out for succinimidide ion (conjugate base anion of succinimide) and phthalimidide ion (conjugate base anion of phthalimide) plus ethyl iodide reactions in acetonitrile–methanol mixtures, and also enthalpy of reaction measurements have been performed for the imidide ion reactions as well as for the carboxylate ion reactions in acetonitrile. Quantitative discussion is given on the reactivity and solvation patterns of imide anions in comparison with these of carboxylate ions.

Results

Rate constants and activation parameters for succinimidide plus ethyl iodide and for phthalimidide plus ethyl iodide reactions are summarized in Table 1. With either of two reactions, rate constant and activation enthalpy indicate very sharp variation over the solvent composition of small content of methanol, followed by a rather mild variation over the other regions, the typically observed feature for the reactions in which a nucleophile–protic solvent interaction determines kinetic behaviour.

Enthalpies of solution for tetramethylammonium salts of succinimidide and of phthalimidide, and for uncharged reaction products, *N*-ethylsuccinimide and *N*-ethylphthalimide have also been determined in the same solvent mixtures and are summarized in Table 2. Single ion enthalpies of transfer for an anion from acetonitrile to solvent mixtures, $\Delta H_t^{AN\rightarrow mix}$ have been calculated on the basis of the tetrabutylammonium/tetrabutylborate assumption, and are summarized in Table 3. Transfer enthalpies for transition state anions have been calculated according to a thermodynamic cycle, combining the single ion enthalpies for the anions, the activation enthalpies, and transfer enthalpies of ethyl iodide,[9] and are summarized in Table 3. All the single ion enthalpies, although less pronounced for transition state anions, show a quite sharp decrease over the solvent compositions of low content of methanol, followed by a rather mild increase over other compositions, in a way analogous to the features observed for rate constants and activation enthalpies, while the enthalpies for uncharged reaction products show a rather small and mild increase over the entire compositions. The features could quantitatively be reproduced by eqns. (1) and (2). In the equations, $\Delta H_{t,PHYS}^{AN\rightarrow MeOH}$ and $\Delta H_{t,SI}^{AN\rightarrow MeOH}$ stand

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

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

for the single ion enthalpy of transfer from acetonitrile to methanol due to 'more physical' interaction and that due to specific interaction, K_{se} stands for the equilibrium constant of the solvent-exchange process at the solvation site around a solute, and x_{AN} and x_{MeOH} stand for the mole fraction of acetonitrile and of methanol.[7–11]

The first term of the right hand side of eqn. (1) which expresses the mild response of transfer enthalpy to solvent composition, has been found empirically to simulate the enthalpy for the perchlorate ion, and is likely to contain the contributions from such 'more physical' interactions as cavity term, protophobic interaction, ion–dipole interaction, and dipole–dipole interaction, *etc.*[7–11] The second term which expresses the steep changes over the region of low content of methanol, has been derived on the basis of the assumption of solvent–exchange equilibria at the solvation site around a solute and contains contributions from such specific and 'more chemical' interactions as hydrogen-bonding, charge-transfer and dipole–dipole association interactions.[7–11]

The calculation of the enthalpies, $\Delta H_t^{AN\rightarrow mix}$ were carried out by step-by-step procedures, systematically changing the parameters, K_{se} and $\Delta H_{t,SI}^{AN\rightarrow MeOH}$, 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

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

	Succinimidide + EtI			Phthalimidide + EtI		
x_{MeOH}	10^4 k/dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	10^4 k/dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
0	1.65×10^3	58.4	−67.4	6.43×10^2	62.6	−61.4
0.1	3.51×10	79.9	−28.5	2.35×10	79.4	−33.5
0.25	8.63	82.4	−31.9	6.14	82.5	−34.4
0.50	2.56	85.6	−31.4	1.87	83.8	−40.0
0.75	1.17	87.8	−30.7	0.874	88.8	−29.8
1.0	0.474	92.4	−23.0	0.357	91.6	−28.0

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

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

x_{MeOH}	Tetramethylammonium succinimidide	Tetramethylammonium phthalimidide	*N*-Ethylsuccinimide	*N*-Ethylphthalimide
0	16.7	18.5	−0.49	19.5
0.1	−13.75	−3.74	—	19.7
0.25	−16.6	−6.39	−0.46	20.15
0.50	−13.9	−3.94	0.75	21.2
0.75	−9.26	−0.16	2.69	22.9
1.0	−0.09	5.82	6.79	25.6

Table 3 Single ion enthalpies of transfer from acetonitrile to solvent mixtures and interaction parameters (kJ mol^{-1})

x_{MeOH}	Succinimidide ion	Phthalimidide ion	TS anion (Succinimidide + EtI)	TS anion (Phthalimidide + EtI)
0	0	0	0	0
0.1	−29.55	−21.3	−8.1	−4.5
0.25	−32.0	−23.6	−8.1	−3.8
0.50	−30.25	−22.1	−3.5	−1.3
0.75	−26.3	−19.0	2.2	6.3
1.0	−19.5	−15.4	12.9	12.0
$\Delta H_{t,PHYS}^{AN \to MeOH}$	17.5	10.6	26.9	20.0
$\Delta H_{t,SI}^{AN \to MeOH}$	−37.0	−26.0	−14.0	−8.0
K_{se}	50.0	60.0	30.0	40.0
Z	3.0	2.4	1.2	0.9

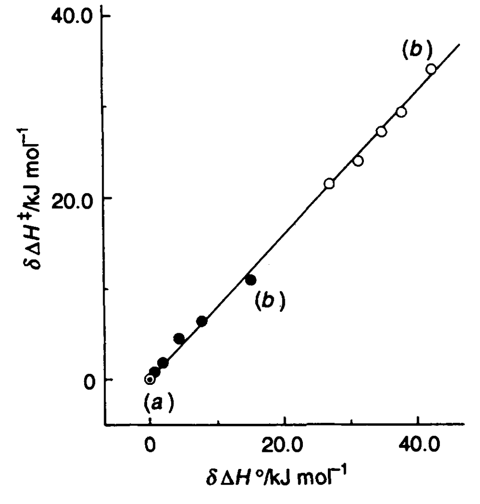

Fig. 1 Activation ethalpy *vs.* reaction enthalpy correlations for the reaction of succinimidide plus ethyl iodide in acetonitrile–methanol mixtures: ○, overall quantity; ●, 'more physical' interaction quantity; (*a*) acetonitrile; (*b*) methanol

maximum deviation, ± 1 kJ mol^{-1} for nucleophiles and ± 3 kJ mol^{-1} for transition state anions. The parameters obtained are also summarized in Table 3. With uncharged reaction products the dissection of transfer enthalpies into constituent terms by the equations did not lead to any definite conclusion on whether the hydrogen-bonding interaction between the imide and methanol makes a significant contribution to the enthalpy, since no definite minimum was found in the transfer enthalpy *vs.* solvent composition profile. Furthermore, the transfer enthalpies for *N*-ethylsuccinimide and for *N*-ethylphthalimide show rather small and mild variation over the entire ranges of solvent composition (see Table 2). Here is seen the most characteristic difference in solvation patterns between anions and uncharged reaction products, even though they are comprised of the same hydrocarbon moieties.

Discussion

Empirical correlations between activation and reaction parameters have often been invoked as the procedures for deriving a transition state index in physical organic chemistry.[5-12] Solvent effects on the enthalpy of reaction for these reactions can be evaluated according to a thermodynamic cycle, by combining the transfer enthalpies for the uncharged reaction product, iodide ion,[9] ethyl iodide,[9] and the nucleophile; one of the correlations is shown in Fig. 1.

Observed effects of solvents on activation and on reaction parameters, δY^* are composite of 'more physical' and a specific interaction quantities, and are given by eqn. (3), where Y refers

$$\delta\Delta Y^* = \delta\Delta Y^*_{PHYS} + \Delta Y_{t,SI}^{AN \to mix}(X^-) - \Delta Y_{t.SI}^{AN \to mix}(Nu^-) \qquad (3)$$

to a relevant thermodynamic quantity,[7,8] superfix * refers to a superfix, ‡ or °; X to a transition state anion or iodide ion, according to the process in consideration.

The transfer enthalpy due to a specific interaction is given by eqn. (4). Hence solvent effects on the activation and reaction

$$\Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{mix}} = \Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}} K_{\mathrm{se}} x_{\mathrm{MeOH}}/(x_{\mathrm{AN}} + K_{\mathrm{se}} x_{\mathrm{MeOH}}) \quad (4)$$

enthalpy due to 'more physical' interaction can be calculated by the following procedure; first, by substituting relevant parameters given in Table 3 into eqn. (4), and then by substituting the calculated values of $\Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{mix}}$ into eqn. (3) (the specific interaction enthalpies for iodide ion are given in ref. 13). The correlation using 'more physical' interaction quantities is also shown in Fig. 1. For the reaction of succinimidide plus ethyl iodide, two types of correlation, although quite fortuitous, practically fall into one correlation of slope 0.79. As the reaction proceeds, the negative charge which has originally been dispersed over an imidide ion becomes more localized on iodide ion. The effects are reflected in the decrease of 'more physical' interaction enthalpy from 17.5 for succinimidide ion to 6.28 kJ mol^{-1} for ethyl succinimide and on the increase from −1.6 for ethyl iodide[9] to 23.7 kJ mol^{-1} for iodide ion.[9] Hence the enthalpy for the transition state anion, 26.9 kJ mol^{-1}, is a combination of the decreasing and of the increasing functions along the reaction coordinate. The coincident slope value from two types of correlations (see Fig. 1) may well be taken as the transition state index. However, the molecular mechanistic interpretation of the slope value will have to be reserved, until functional dependence of the enthalpy along the reaction coordinate is evaluated by any other means.

Linear correlations between activation enthalpies and activation entropies, have also been invoked as another type of empirical procedure for deriving a transition state index, and although the credibility of the classical form has been scrutinized mainly from viewpoints of statistics,[12,14,15] recently the correlation has been developed to a thermo-kinetical method for evaluating the solvation number of nucleophile and of transition state anion.[7,8] One such classical correlation is shown in Fig. 2.

The entropy of transfer due to a specific interaction is given by eqn. (5), and the specific interaction enthalpy, $\Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}}$ is the product of the number of methanol molecules participating in the hydrogen-bonding interaction with an anion, Z and the enthalpy change of solvent exchange process on the solvation site around an anion, ΔH_{se}, eqn. (6).[7-11]

$$\Delta S_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{mix}} = \left(\frac{Z\Delta H_{\mathrm{se}}}{T}\right)\left(\frac{K_{\mathrm{se}} x_{\mathrm{MeOH}}}{x_{\mathrm{AN}} + K_{\mathrm{se}} x_{\mathrm{MeOH}}}\right) + ZR\ln(x_{\mathrm{AN}} + K_{\mathrm{se}} x_{\mathrm{MeOH}}) \quad (5)$$

$$\Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}} = Z\Delta H_{\mathrm{se}} \quad (6)$$

When the specific interaction enthalpy, $\Delta H_{\mathrm{t,SI}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}}$ is dissected into its constituent terms, Z and ΔH_{se}, transfer entropy due to specific interaction can be calculated by substituting the parameters summarized in Table 3 into eqn. (5), and activation entropies due to 'more physical' interaction can be evaluated by substituting the results into eqn. (3). Calculations were repeated step-by-step systematically changing the solvation numbers for nucleophile and transition state anion, $Z(\mathrm{Nu}^-)$ and $Z(\mathrm{TS}^-)$, until a linear correlation holds between physical interaction quantities, $\delta\Delta H^{\ddagger}_{\mathrm{PHYS}}$ and $\delta\Delta S^{\ddagger}_{\mathrm{PHYS}}$. The final correlation is shown in Fig. 2. One of the most plausible sets of solvation numbers is summarized in Table 3 and the slopes of the correlation, the isokinetic temperature due to 'more physical' interaction, β_{PHYS} are summarized in Table 4.

So far, sets of parameters which characterize the reactivity and solvation patterns, have been derived and a consistency check of the parameters is desirable before proceeding further. This will be accomplished by the back calculation of activation enthalpy and of activation entropy, which can be carried out by three procedures: (1) values of activation enthalpy due to 'more physical' interaction can be derived by substituting the relevant parameters summarized in Table 3 and transfer enthalpies for ethyl iodide[9] into eqn. (7); (2) activation entropy due to 'more physical' interaction can be derived substituting the above results and β_{PHYS} into eqn. (8); (3) substitution of the above results and of the calculated values of transfer enthalpy and of entropy due to specific interaction into eqn. (3), which have been derived by substituting the relevant parameters given in Table 3 into eqns. (4) and (5), lead to the desired quantities. Comparison of the back-calculated values with experimental results is shown in Fig. 2. The calculated values simulate well the pattern shown by experimental quantities. In addition, a non-linear or skewed S-shape character of an activation enthalpy *vs.* activation entropy correlation is confirmed. The substitution of the calculated values of $\delta\Delta H^{\ddagger}$ and of $\delta\Delta S^{\ddagger}$ into eqn. (9) gives the value, $\delta\Delta G^{\ddagger}$, and this enables the consistency check of the parameters to be carried out in terms of the correlation of $\delta\Delta H^{\ddagger}$ *versus* $\delta\Delta G^{\ddagger}$, which is recommended on the basis of statistics.[14] The set of parameters summarized in Tables 3 and 4 confirmed non-linear character of $\delta\Delta H^{\ddagger}$ *versus* $\delta\Delta G^{\ddagger}$ correlation. The characterization of these empirical correlations through simulation is well beyond the scope of statistical analysis on an enthalpy *vs.* entropy and an enthalpy *vs.* free energy correlation[12,14,15] so far carried out.

$$\delta\Delta H^{\ddagger}_{\mathrm{PHYS}} = [\Delta H_{\mathrm{t,PHYS}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}}(\mathrm{TS}^-) - \Delta H_{\mathrm{t,PHYS}}^{\mathrm{AN}\rightarrow\mathrm{MeOH}}(\mathrm{Nu}^-)]x_{\mathrm{MeOH}} [1 - 1.23x_{\mathrm{MeOH}}(1 - x_{\mathrm{MeOH}})] - \Delta H_{\mathrm{t}}^{\mathrm{AN}\rightarrow\mathrm{mix}}(\mathrm{EtI}) \quad (7)$$

$$\delta\Delta H^{\ddagger}_{\mathrm{PHYS}} = \beta_{\mathrm{PHYS}}\,\delta\Delta S^{\ddagger}_{\mathrm{PHYS}} \quad (8)$$

$$\delta\Delta G^{\ddagger} = \delta\Delta H^{\ddagger} - T\delta\Delta S^{\ddagger} \quad (9)$$

Since the two types of correlation shown in Fig. 1 are practically linear and of similar slope values, then the specific effects brought about by a particular interaction, 'more physical' or a specific interaction, on activation and/or reaction parameters, would not successfully be uncovered by these procedures. Thus, the procedures leading to the correlations shown in Fig. 2 provide a more stringent test for evaluating the role of these effects on activation quantities.

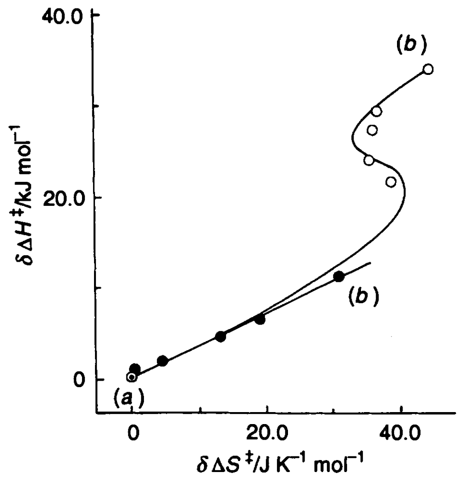

Fig. 2 Activation enthalpy *vs.* activation entropy correlations for the reaction of succinimide ion plus ethyl iodide in acetonitrile–methanol mixtures: ○, overall quantity; ●, 'more physical' interaction quantity, (—), calculated values (see text), (*a*), acetonitrile; (*b*), methanol

Table 4 Comparison of the characteristics of imidide ion and carboxylate ion reactions[a]

Reaction	$\mathrm{p}K_a$ in H_2O	$2 + \log k_{AN}$	$\Delta H^{\ddagger}_{AN}$	β_{PHYS}/K	$\Delta H^{AN \rightarrow MeOH}_{t,SI}(Nu^-)$	$\Delta H^{AN \rightarrow MeOH}_{t,SI}(TS^-)$	ΔH°_{AN}
Succinimidide + EtI	9.66[b]	1.22	58.4	355	−37.0	−14.0	−138.3
Phthalimidide + EtI	8.30[c]	0.81	62.6	406	−26.0	−8.0	−134.7
Pivalate + EtI	5.03[d]	1.46[e]	63.2[e]	360[e]	−43.5[f]	−12.0[e]	−86.5
Benzoate + EtI	4.20[d]	0.68[e]	61.9[e]	340[e]	−36.0[f]	−9.0[e]	−74.2

[a] $\mathrm{p}K_a$s are for the conjugate acids. A suffix, $_{AN}$ indicates the value in acetonitrile. $2 + \log k_{AN}$ values are at 30.0 °C. Enthalpies are in kJ mol^{-1}. [b] Ref. 16. [c] Ref. 17. [d] Ref. 18. [e] Ref. 7. [f] Ref. 11.

$\mathrm{p}K_a$ Values of weak acids in the aqueous phase have often been invoked as the reactivity index (sometimes as the measure of solute–solvent interaction) of the conjugate-bases in empirical energy correlations. For quantitative discussion, various kinetic and equilibrium quantities which could well be suggested as reactivity and solvation index, are summarized in Table 4 for the imidide ion and carboxylate ion reactions. Within a group, either the imidide or carboxylate ion group, aliphatic anions tend to be more basic and more reactive than aromatic anions according to three criteria, $\mathrm{p}K_a$ in H_2O, $\log k_{AN}$, and $\Delta H^{AN \rightarrow MeOH}_{t,SI}$. However, any systematic difference in the kinetic and the equilibrium properties could not be observed between the imidide and carboxylate ion reactions, in contradiction to the expectation based on the significant difference in the $\mathrm{p}K_a$ values in the aqueous phase. One exception is the reaction enthalpy in acetonitrile. The averaged difference in the reaction ethalpy between imidide ion and carboxylate ion reactions, *ca.* 56 kJ mol^{-1} is twice as large as the difference in the energy of ionization in the aqueous phase, *ca.* 25 kJ mol^{-1}.

$\mathrm{p}K_a$ Values in the aqueous phase relate to a partially compensating quantity between heterolytic O–H (or N–H) bond cleavage and hydrogen-bonding between conjugate-base anion and water molecules.[19] The kinetic parameters in acetonitrile and transfer enthalpies due to specific interaction are all related to the partial bonding between an anion and carbon (or hydrogen) atom. The reaction enthalpy in acetonitrile is related to an O–C (or N–C) bond formation. These considerations suggest that empirical correlations between thermodynamic quantities which refer to different molecular processes may well lead to molecular mechanistic information that is not soundly based.

Conclusions

In order for the successful appreciation of the effects from various interactions of different molecular origin on activation and on reaction parameters, more than two types of empirical correlations will have to be analysed on empirical as well as on theoretical grounds. Practical examples are shown in Figs. 1 and 2.

Any essential differences in reaction and in solvation characteristics could not be detected between imidide and carboxylate ions through the experimental procedures, in which the partial bonding between the anion and relevant species is the dominant features of the molecular process concerned. Discrimination between the two types of anions can be accomplished only through procedures in which full bond-making or bond-breaking is the prevailing of molecular process.

Experimental

Materials.—Tetramethylammonium succinimide was prepared from tetramethylammonium hydroxide and succinimide in methanol according to essentially the same procedures as described elsewhere,[20] recrystallized three times from acetonitrile–acetone mixture and dried over phosphorus pentoxide (Found: C, 55.7; H, 9.4; N, 16.15. Calc. for $C_8H_{16}N_2O_2$: C, 55.79; H, 9.36; N, 16.27%). Tetramethylammonium phthalimidide was prepared similarly from tetramethylammonium hydroxide and phthalimide in methanol, recrystallized three times from acetonitrile, and dried over phosphorus pentoxide (Found: C, 65.4; H, 7.4; N, 12.8. Calc. for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.71%). Other materials were treated as described elsewhere.[7]

Product Analysis and Kinetics.—Stock solutions of ethyl iodide and of tetramethylammonium succinimidide were mixed in tightly stoppered flasks. After *ca.* ten half-lives, the solvents and the unreacted ethyl iodide were removed carefully at reduced pressure. The solid precipitate which formed was washed with several portions of ether and the extracted compound was chromatographed on silica gel in ether. The ^1H NMR spectra of both crude and chromatographed samples were comparable; $\delta(CDCl_3)$ 3.52 (2 H, q, *J* 7), 2.65 (4 H, s), 1.15 (3 H, t, *J* 7) (Found: C, 56.3;, H, 7.2; N, 11.4. Calc. for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.02%).

Stock solutions of ethyl iodide and of tetramethylammonium phthalimide were mixed in a tightly stoppered flask. After *ca.* ten half-lives, solvents and the unreacted ethyl iodide were removed carefully under reduced pressure. The solid precipitate which formed was washed with several portions of ether and the extracted compound was recrystallized three times from water–ethanol mixture. The ^1H NMR spectra of both crude and recrystallized samples were comparable: $\delta(CDCl_3)$ 7.9–7.7 (4 H, m), 3.72 (2 H, q, *J* 7), 1.27 (3 H, t, *J* 7) (Found: C, 68.3; H, 5.0; N, 8.0. Calc. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00%). The results are consistent with the predominant alkylation at nitrogen atom in nucleophiles.

Aliquots (5 cm^3) from stock solutions of ethyl iodide and of relevant tetramethylammonium imidides were mixed in tightly stoppered glass test tubes and the mixtures were kept in a thermostatted bath. After a given time, the reaction mixture was poured into a hexane–water mixture. The amount of iodide ion formed was determined with potentiometric titration using silver nitrate solution. The rate measurements were carried out at four of the following temperatures, 20.0, 30.0, 40.0, 50.0 and 60.0 °C. The experimental errors were estimated to be *ca.* 2% for rate constants, 1 kJ mol^{-1} for activation enthalpies, and 3 J K^{-1} mol^{-1} for activation entropies.

Heats of Solution Measurements.—Heats of solution were measured at 25.0 ± 0.1 °C with Tokyo Riko twin isoperibol calorimeter. Final concentration ranges of solutes were 0.4×10^{-2}–2.5×10^{-2} dm mol^{-1} and experimental errors were *ca.* 0.7 kJ mol^{-1}.

Heats of Reaction Measurements.—Heats of reaction were measured at 25.0 ± 0.2 °C by either of two ways. *Method 1.* A known amount of relevant tetramethylammonium salt (usually 4.4×10^{-4} mol) was dissolved in acetonitrile (100 cm^3). A large excess of ethyl iodide over the salt (usually 9×10^{-3} mol) together with acetonitrile (usually 1 cm^3) was sealed in an ampoule. The salt solution and the ethyl iodide solution sealed in an ampoule were kept in the calorimeter. After thermal equilibration, the ampoule was broken and the heat evolved was measured. *Method 2*. A known amount of relevant tetramethylammonium salt (usually 4.4×10^{-4} mol) was sealed in an ampoule. Large excess of ethyl iodide over the salt (usually 9×10^{-3} mol) was dissolved in acetonitrile (100 cm^3). The solution and the salt sealed in an ampoule were kept in the calorimeter. After thermal equilibration the ampoule was broken and the heat evolved was measured. In the calculation of enthalpy of reaction, heat of dilution of ethyl iodide solution (for the first case) or heat of solution of relevant salt (for the second case) was corrected. The experimental errors were estimated to be *ca.* 2 kJ mol^{-1} from three to four measurements. Results are summarized in Table 4.

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