Reaction of Triphenylphosphine with Methyl Iodide. Transfer Thermodynamic Quantities and Various Extended Brönsted Treatments

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The enthalpies of solution and the apparent molar volumes have been determined in various solvents for the reactants and products of the reaction of triphenylphosphine with methyl iodide in various solvents. The rate constants, activation enthalpies, activation volumes, and the reaction enthalpies have also been determined for these reactions. Three types of extended Brönsted plots, *i.e.*, $\Delta V^\ddagger$ *versus* ΔV°, $\delta \Delta H^\ddagger$ *versus* $\delta \Delta H^\circ$ with solvent variation, and $\Delta H^\ddagger$ *versus* ΔH° with variation of the nucleophile, do not show any general pattern of behaviour. The physical meaning of the various Brönsted slopes is discussed.

Solvent effects on activation parameters for any given chemical reaction may be dissected into initial-state and transition-state contributions through the determination of the thermodynamics of transfer of the particular reactants[1–6] from one solvent to another. Results of such studies are useful, not only in discussions on the microscopic nature of reaction mechanisms, but also in the understanding of rate–equilibrium relationships.[7–15] When ionic species take part in the given reaction, it is convenient to use an extra thermodynamic assumption in order to obtain single-ion transfer quantities. No extra thermodynamic assumption has been proved to yield the 'correct' single-ion quantities, but the tetraphenylarsonium–tetraphenylborate assumption has been widely used and discussed.[16–19] In the Menschutkin-type reaction of triphenylphosphine with methyl iodide, the reactants pass through a dipolar transition state to the product cation and anion, $Ph_3\overset{+}{P}Me$ and I^-. Although no extra thermodynamic assumption is involved with respect to the dipolar transition state, it is again useful to discuss the transfer quantities of the product in terms of an extra thermodynamic assumption.

In this work, we determine activation parameters in various solvents for reaction (1), together with transfer thermodynamic

$$(C_6H_5)_3P + CH_3I \longrightarrow (C_6H_5)_3\overset{+}{P}CH_3 + I^- \quad (1)$$

parameters of the reactants and products, and we discuss the possible physical meaning of the values of the slopes in various extended Brönsted relationships that we construct.

Experimental

Materials.—Triphenylphosphine was recrystallized three times from ethyl alcohol and dried (P_2O_5) for a few days. Methyltriphenylphosphonium iodide, prepared from triphenylphosphine and methyl iodide in ether, was recrystallized three times from propan-2-ol and dried (P_2O_5) for a few days (Found: H, 4.5; C, 56.5; I, 31.3. Calc. for $C_{19}H_{18}IP$: H, 4.5; C, 56.5; I, 31.4%). Other materials were treated as described previously.[20–23]

Heats of Solution and Heats of Reaction Measurements.—Heats of solution were measured at 25.0 °C with a twin isothermal calorimeter (Tokyo Riko TIC-2D);[23–25] the final concentrations used for measurements were *ca.* 0.8—1.2 × 10^{-2} for salts and triphenylphosphine, 3.5 × 10^{-2} for pyridine, and 6.1 × 10^{-2} mol dm^{-3} for triethylamine. The heat of reaction of triphenylphosphine with methyl iodide was measured at 25 °C with a Tokyo Riko MPC-11 calorimeter used as a conduction type of vessel. Triphenylphosphine solution (0.082 1 g of triphenylphosphine dissolved in 1.2 cm^3 of acetonitrile) was sealed in an ampoule and 25 cm^3 of methyl iodide solution in acetonitrile (2.4 × 10^{-2} mol dm^{-3}) were placed in a calorimeter cell. After thermal equilibration, the heat of reaction was measured as described previously.[22]

For reactions of methyl iodide with neutral nucleophiles other than triphenylphosphine, the heats of reaction were also measured with the twin isothermal calorimeter (TIC-2D) at 25 °C. A known amount of nucleophile (*ca.* 1.5 × 10^{-3} mol) was dissolved in acetonitrile (1.5 cm^3) in an ampoule, the ampoule sealed, and then placed in the calorimeter cell with methyl iodide solution (100 cm^3) (2—10 times the equivalent of the nucleophile dissolved in acetonitrile). After thermal equilibration, the heats of reaction were measured by the same procedures as used for the heats of solution measurements.[23–25]

For the reaction of methyl iodide with bromide ion, the heat of reaction was measured two ways. First, a known amount of tetrabutylammonium bromide (*ca.* 1.0 × 10^{-3} mol) was sealed in an ampoule, which was placed in the calorimeter cell with methyl iodide solution (100 cm^3) (*ca.* 40 times the equivalent of the nucleophile dissolved in acetonitrile); after thermal equilibration, the heats of solution were measured. Secondly, a known amount of methyl iodide (*ca.* 1.6 × 10^{-2} mol) was sealed in an ampoule, which was placed in the calorimeter cell with 100 cm^3 of a known concentration of tetrabutylammonium bromide solution (*ca.* 1.0 × 10^{-2} mol dm^{-3}); after thermal equilibration, the heats of solution were measured. In both cases, measured values agreed with the heats of solution values of the respective species in pure acetonitrile, within experimental errors, although the reaction went to completion during the process.

Kinetics at Atmospheric and High Pressures, and Density Measurements.—These measurements were carried out as described elsewhere.[20,21]

Results and Discussion

Single Ion Enthalpies of Transfer and Solvation Change during the Reaction.—Enthalpies of solution of the reactants and products for the reaction of triphenylphosphine (TPP) with methyl iodide (MeI) have been determined in four dipolar aprotic solvents [acetonitrile (AN), propylene carbonate (PC), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA)] and are summarized in Table 1. Enthalpies of solution have also been determined for the relevant species of the three Menschutkin-type reactions with methyl iodide, *i.e.*, pyridine plus methyl iodide, *N,N'*-dimethylimidazolidine-2-thione (DMIT) plus methyl iodide, and triethylamine (TEA) plus

Table 1. Enthalpies of solution at 25.0 °C (kJ mol^{-1})

Solvent	MeI	DMIT	Pyridine	TEA	TPP	MeDMIT$^+$I$^-$ [a]	MePyr$^+$I$^-$ [b]	MeTEA$^+$I$^-$ [c]	MeTPP$^+$I$^-$ [d]
AN	3.63 [e]	19.6 [e]	1.64 [f]	5.30 [f] (5.5 [g])	26.1	12.8 [e]	10.5 [f]	9.14 [f]	11.5
PC	3.28 [e]	20.3 [e]	0.77	6.15 (6.5 [g])	22.9	17.5 [e]	14.25	13.9	13.6
DMF	0.80	18.4	−0.38	5.34 (5.3 [g])	18.4	8.57	1.72	3.17	−5.18
DMA	0.23 [h]	17.8 [h]	−0.88	5.155	16.6	11.7 [h]	4.03	6.86	−5.95

[a] MeDMIT$^+$I$^-$, methyl iodide salt of *N,N'*-dimethylimidazolidine-2-thione. [b] MePyr$^+$I$^-$, methyl iodide salt of pyridine. [c] MeTEA$^+$I$^-$, methyl iodide salt of triethylamine. [d] MeTPP$^+$I$^-$, methyl iodide salt of triphenylphosphine. [e] Ref. 23. [f] Ref. 26. [g] Ref. 27. [h] Ref. 24.

Table 2. Transfer enthalpies and slope values (*Sl*) at 25.0 °C (kJ mol^{-1})

Solvent	MeI	DMIT	Pyridine	TEA	TPP	MeDMIT$^+$	MePyr$^+$	MeTEA$^+$	MeTPP$^+$	(Bu^n)$_4$N$^+$ [a]	I$^-$ [a]
AN	0	0	0	0	0	0	0	0	0	0	0
PC	−0.35	0.7	−0.9	0.85	−3.2	−1.05	−2.0	−1.0	−3.65	−0.65	5.75
DMF	−2.8	−1.2	−2.0	0.0	−7.7	−6.0	−10.6	−7.8	−18.5	−8.2	1.8
DMA	−3.4	−1.8	−2.5	−0.15	−9.5	−7.8	−13.2	−9.0	−24.15	−11.3	6.7
Sl	0.32	0.15	0.23	0.0	0.87	0.7	1.20	0.86	2.2	≡1.0	

[a] Ref. 25.

methyl iodide, in the same four solvents for comparison. These are also summarized in Table 1.

From these values transfer enthalpies can be calculated for neutral species without recourse to any assumptions. Single-cation transfer enthalpies have been calculated by subtracting the iodide ion transfer enthalpies from the transfer enthalpies determined for the salts, using our previous tetrabutylammonium–tetrabutylborate ion assumption.[25] All values are summarized in Table 2.

For most of the species included in Table 2, transfer enthalpies indicate a general exothermic trend along the series acetonitrile, propylene carbonate, *N,N*-dimethylformamide, and *N,N*-dimethylacetamide. This trend can be quantitatively expressed using linear regression analysis on the transfer enthalpies of the reference cation, tetrabutylammonium ion, equation (2). The slope values, *Sl*, for the relevant species are

$$\Delta H_t^{\mathrm{AN}\rightarrow\mathrm{S}}(\mathrm{X}) = Sl\cdot\Delta H_t^{\mathrm{AN}\rightarrow\mathrm{S}}(\mathrm{Bu_4N^+}) \qquad (2)$$

also indicated in the bottom row of Table 2. As is shown by its large *Sl* value, triphenylphosphine is more sensitive to solvent variation than the other nucleophiles. As triphenylphosphine also has a large molar volume (see Table 4), either a particularly large cavity term or a surface area effect could be responsible. The similarity in the *Sl* values of triphenylphosphine and the tetrabutylammonium ion, *i.e.*, 0.87 *versus* 1.0, indicate, in turn, that the cationic charge in the reference cation is sufficiently shielded by four butyl groups for the charge effect on transfer enthalpies to be undetected.

In the Menschutkin-type reactions of methyl iodide, the methyl group in methyl iodide is incorporated in the product cation, while the iodine atom becomes iodide ion. Thus, the difference in the slope values, Δ*Sl*, as defined by equation (3),

$$\Delta Sl = Sl_{\mathrm{cation}} - (Sl_{\mathrm{Nu}} + \tfrac{1}{2}Sl_{\mathrm{MeI}}) \qquad (3)$$

where Sl_{cation}, Sl_{Nu}, and Sl_{MeI} are the slope values of cation, nucleophile, and methyl iodide, respectively, can serve as the index that describes the solvation change around the incipient cationic moiety during the reaction. The values increase in the order 0.39, 0.70, 0.81, and 1.2 for *N,N'*-dimethylimidazolidine-2-thione, triethylamine, pyridine, and triphenylphosphine, for each reaction with methyl iodide. The observed solvent effects on these Menschutkin-type reactions can then be analysed into the solvation change around the respective incipient cationic and anionic moieties. The relative significance of the contribution around the incipient cationic moiety increases in the order given above, since the anion (iodide ion) is common to all the reactions. In other words, for the triphenylphosphine plus methyl iodide reaction, on transfer from acetonitrile to *N,N*-dimethylacetamide, the ratio of the solvation change around the incipient cationic moiety to that around the incipient anionic moiety during the reaction is evaluated as given in expression (4), in kJ mol^{-1}. This indicates that for the triphenylphosphine

$$\Delta Sl\cdot\Delta H_t^{\mathrm{AN}\rightarrow\mathrm{DMA}}(\mathrm{Bu_4N^+}):[\Delta H_t^{\mathrm{AN}\rightarrow\mathrm{DMA}}(\mathrm{I^-}) - \tfrac{1}{2}\Delta H_t^{\mathrm{AN}\rightarrow\mathrm{DMA}}(\mathrm{MeI})] = 1.2\times(-11.3):8.4 \qquad (4)$$

reaction the solvation change around the incipient cationic moiety exceeds that of the anionic moiety. With these procedures, three phenyl groups are shown to be insufficient to shield the central cationic charge from the surrounding solvent molecules. The larger polarizability of the phenyl group could be responsible.

Table 3. Rate constants and activation enthalpies for the reaction of triphenylphosphine with methyl iodide at 30 °C

Solvent	10^4k/dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}
Propylene carbonate	169.3	48.3
Acetonitrile	76.4	47.4
N,N-Dimethylacetamide	108.5	44.6
N,N-Dimethylformamide	147.4	45.8
Nitrobenzene	90.8	
Methanol	23.7	
Cyclohexanone	43.9	
Methyl ethyl ketone	28.3	
Tetrahydrofuran	15.45	
Bromobenzene	18.7	
Propan-2-ol	10.6	
Benzene	5.48	
Di-isopropyl ether	0.691	

Solvent Effects on the Rate Constants.—The rate constants and the activation enthalpies for the reaction of triphenylphosphine with methyl iodide measured in various solvents are summarized in Table 3.

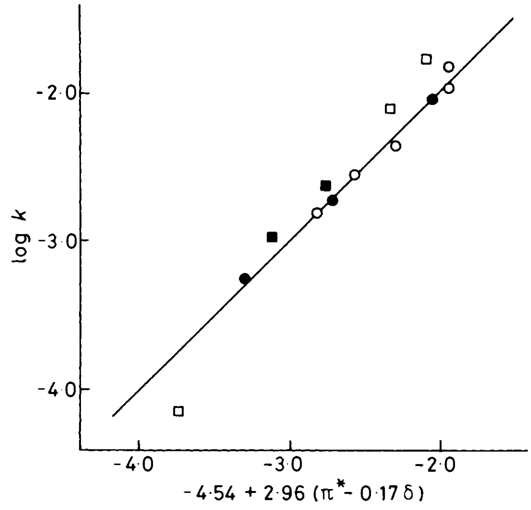

Figure 1. Plots of observed *versus* calculated values of solvent effects on log *k* for the reaction of triphenylphosphine with methyl iodide at 30 °C. ○ and □, aliphatic solvents; ●, aromatic solvents; and ■, protic solvents

Recently, α, β, and π* scales of empirical solvent parameters have been developed and used extensively for correlating various phenomena in solution.[28,29] Solvent effects on the rate of reaction of tripropylamine plus methyl iodide have been expressed by equation (5).[30]

$$\log k = -4.18 + 4.66\,(\pi^* - 0.086\,\delta) \qquad (5)$$

The rate constants measured in eight solvents, open and filled circles in Figure 1, are correlated by equation (6).

$$\log k = -4.54 + 2.96\,(\pi^* - 0.17\,\delta) \qquad (6)$$
$$r = 0.995$$

The tripropylamine reaction is more sensitive to solvent variation than the triphenylphosphine reaction; the sensitivity ratio is 4.66:2.96. The activation enthalpy *versus* reaction enthalpy correlations with the nucleophile variation are shown in Figure 3. In these correlations, aliphatic amines form one series, the aliphatic series, while triphenylphosphine belongs to the other series, the aromatic series, and the sensitivity ratio for aliphatic to aromatic series is 0.34 : 0.23. Thus, the lower sensitivity of the reaction of triphenylphosphine with methyl iodide than that of an aliphatic amine has consistently been shown by two procedures, solvent variation and structural variation. Furthermore, the extended Brönsted treatment of the solvent effects on activation enthalpies, $\delta\ \Delta H^\ddagger$, *versus* reaction enthalpies, $\delta\ \Delta H^\circ$, which have been calculated from the enthalpies of solution included in Table 1 through a thermodynamic cycle, gives a slope value, of 0.22, which is nearly the same as is observed in Figure 3.

A dδ term was originally introduced to incorporate the solvatochromic effect* of the dye into the α, β, π*, scheme, which indicates a hypsochromic shift,[31,32] and can be regarded as an index of the contribution due to the orientation of solvent molecules around the dipolar solute.[33] At first sight, one would be quite sceptical about the significance of the dδ terms in equations (5) and (6), since the values look so small. The significance of the term can be confirmed in two ways: firstly, the use of 0.086 δ instead of 0.17 δ in equation (6) decreases the correlation coefficient from 0.995 to 0.961; secondly, the substitution of 0.086 δ in equation (6), in place of 0.17 δ, leads to a 1.8-fold increase in the rate constants, which far exceeds the experimental error for the rate constants, ±2%.

In Menschutkin-type reactions, solvent molecules surrounding the reacting molecules will reorientate as a result of polarity changes during the reaction. The orientation effect brought about around the region of the incipient cationic moiety would be most significant for the triphenylphosphine reaction, as is inferred from the large Δ*SI* value indicated above. Thus, the close similarity of the ratio of the dδ values, 0.086:0.17, for the tripropylamine to triphenylphosphine reaction to the ratio of the Δ*SI* values, 0.70: 1.2, for triethylamine to triphenylphosphine reaction is not an artifact of the treatment but indicates the significance of solvent reorientation around the incipient cationic moiety during the reaction.

Table 4. Apparent molar volumes, reaction volumes, and activation volumes at 30 °C (cm^3 mol^{-1})

	φ_v				
Solvent	MeI	TPP	MeTPP$^+$I$^-$	$\Delta\varphi_v$	$\Delta V_0^\ddagger$
AN	67.1	232.6	249.9	−49.8	−28.0
PC	65.1	239.8	276.7	−28.2	−17.6
DMF	62.7	235.2	258.6	−39.3	−21.7
DMA	64.7	233.3	256.6	−41.4	−21.8
	φ_v				
	MeI	TEA	MeTEA$^+$I$^-$	$\Delta\varphi_v$	$\Delta V_0^\ddagger$
AN	67.1	139.4	143.4	−63.1	−28.2
PC	65.1	136.8	165.7	−36.2	−25.8

Activation Volumes and Reaction Volumes.—Activation volumes were determined by the least-squares method, after expanding the rate constant measured at pressure *p* into a power series of the pressure [equations (7) and (8)].

$$\ln k_p = \ln k_0 + Bp + Cp^2 \qquad (7)$$

$$\Delta V_0^\ddagger = (-1)BRT \qquad (8)$$

The apparent molar volumes of the solutes, φ_v, were calculated from equation (9), where the quantities have their

$$\varphi_v = 1\,000\,(d_0 - d)/cd_0 + M_2/d_0 \qquad (9)$$

usual meaning. The reaction volumes were calculated from the apparent molar volumes according to equation (10). These

$$\Delta\varphi_v = \Delta\bar{V}^\circ = \varphi_{v,\text{product}} - (\varphi_{v,\text{Nu}} + \varphi_{v,\text{MeI}}) \qquad (10)$$

values are all summarized in Table 4. The plots of activation volumes *versus* reaction volumes are shown in Figure 2. In previous work, the relationship in equation (11) was derived for the reaction of various nucleophiles with methyl iodide, which included pyridine plus methyl iodide and DMIT plus methyl iodide reactions, for the volume changes measured in acetonitrile and propylene carbonate solvents.[24] The relationship is indicated in Figure 3 as a broken line. The corresponding slope for the triethylamine–methyl iodide reaction is smaller, and that for the triphenylphosphine–methyl iodide reaction is larger, than that given in equation (11).

$$\Delta V_0^\ddagger = 0.33\,\Delta\varphi_v - 9.2\,(\text{cm}^3\,\text{mol}^{-1}) \qquad (11)$$

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* The shift in the wavelength of the absorption maximum of the dye on changing the solvent.

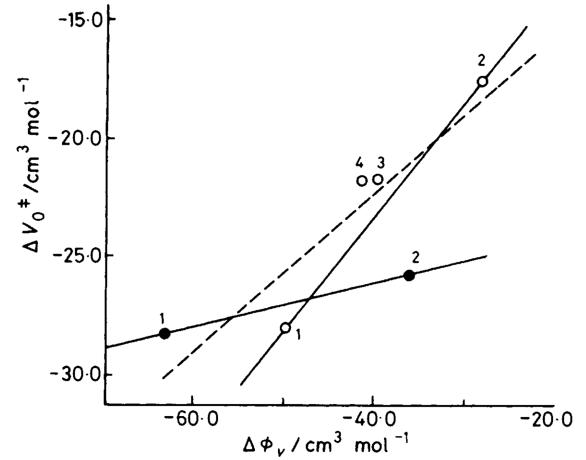

Figure 2. Correlations of activation volumes with reaction volumes. ○, TPP + MeI; ●, triethylamine + MeI. 1, AN; 2, PC; 3, DMF; and 4, DMA

For all of the nucleophile and product cation pairs that we have studied, solvent variation from acetonitrile to propylene carbonate does not lead to a substantial change in stability, *i.e.*, the transfer enthalpy is rather small (see Table 2). Thus the solvent effects on the activation volumes as well as on the reaction volumes, and the slope value, 0.33, in equation (10), would mostly be ascribed to the solvation change around the incipient iodide ion. However, this does not apply to the triphenylphosphine plus methyl iodide reaction, as the transfer enthalpy of the product cation is significantly negative, even for the transfer from acetonitrile to propylene carbonate, −3.6 kJ mol^{-1}. Thus the solvation change during this particular reaction is by far the largest of the reactions we have studied. The significance of solvation changes around the incipient cationic moiety in determining the Brönsted slope value can be evaluated in another way. The results in *N,N*-dimethylformamide and *N,N*-dimethylacetamide solvents deviate, in that order, from the regression line. The order in deviation coincides with the order of stability increase of the cation, as indicated by transfer enthalpies (see Table 2).

Since the transfer enthalpies of the triethylamine plus methyl iodide reaction are not in any way irregular, another reason for the low Brönsted slope must be sought. In acetonitrile + methanol mixtures, the isokinetic temperature due to physical interaction, β_{phys}, has been determined for three reactions, DMIT, pyridine, and triethylamine, each with methyl iodide. The first two reactions, for which the volume correlation conforms to equation (10), have β_{phys} higher than room temperature, while for the last reaction β_{phys} lies below room temperature.[26] The magnitude of the isokinetic temperature determines the relative contribution of enthalpy *versus* entropy term in the activation process and therefore must have a direct bearing on the magnitude of the activation volume.

The volume correlation provides a very sensitive way of detecting solvation changes during the reaction, since energies accompanying the volume correlation are quite small compared with those accompanying the other types of empirical energy correlations. Hence, only under very limited conditions can unambiguous physical information be drawn from volume correlations on solvation changes.

Activation Enthalpy and Reaction Enthalpy Correlation.—Activation enthalpies and reaction enthalpies for various reactions of nucleophiles plus methyl iodide are summarized in Table 5. The results in reference 34 contained some misprints and the correct values are shown in Table 5. The results for the reactions of triphenylphosphine plus methyl iodide and 4-dimethylaminopyridine plus methyl iodide, determined in this work, fall around the regression line determined by Arnett and Reich,[34] the line drawn through the open circles in Figure 3, and we will refer to this group as the 'aromatic series.' Aliphatic amines and thione derivatives are likely to form another series, filled circles in Figure 3, and they will be referred to as the 'aliphatic series.' As is obvious from Figure 3, the aromatic and aliphatic series are likely to have a common intercept at zero reaction enthalpy. The bromide ion plus methyl iodide reaction forms another series by itself. The type of charge of the reaction, together with the accompanying solvation change during the reaction, could be responsible for the difference in the intercept.

Table 5. Activation enthalpies and reaction enthalpies in acetonitrile (kJ mol^{-1})

Nucleophile	$\Delta H^{\ddagger}$	ΔH°
'Aromatic series'		
Pyridine[a]	54.2	−97.9
3-Bromopyridine[a]	57.8	−75.8
3-Chloropyridine[a]	58.0	−80.7
4-Cyanopyridine[a]	60.3	−74.9
3,5-Dichloropyridine[a]	61.7	−65.6
2-Chloropyridine[a]	66.0	−53.2
4-Dimethylaminopyridine	47.8	−113.4
Triphenylphosphine	47.4	−137.2
'Aliphatic series'		
N,N-Dimethylimidazolidine-2-thione[b]	60.5	−49.8
1-Ethyl-3-methyl-4-imidazoline-2-thione[c]	55.2	−59.8
N,N,N',N'-Tetramethylthiourea[d]	53.5	−70.3
2,3-Dihydro-1,2,5-trimethyl-1,2,4-Triazole-3-thione	51.3	−69.7
N-Methylpiperidine	39.2	−117.0
Triethylamine	36.6	−120.5
1,4-Diazabicyclo[2.2.2]-octane	33.1	−121.6
Quinuclidine	29.7	−135.2
Bromide ion	69.1	*ca.* 0

[a] Ref. 34. [b] Ref. 23. [c] Ref. 24. [d] Ref. 22.

The common intercept should be taken as an experimentally determined activation enthalpy at zero reaction enthalpy, $\Delta H_0^{\ddagger}$, or as an intrinsic barrier for the neutral nucleophile plus methyl iodide reaction, in the terms used by Marcus and the elaborated version of rate–equilibrium theory.[7,14,35,36] An intrinsic barrier has been evaluated here as $\Delta H_0^{\ddagger} = 77.0$ kJ mol^{-1}. The theoretical values were calculated from the conventional form of the Marcus theory, equation (12),[7,14] as well as for the integrated form of the symmetry principle, equation (13),* all of

$$\Delta H^{\ddagger} = \Delta H_0^{\ddagger}\,(1 + \Delta H^{\circ}/4\,\Delta H_0^{\ddagger})^2 \qquad (12)$$

$$\Delta H_0^{\ddagger 2} = \Delta H^{\ddagger}\,(\Delta H^{\ddagger} - \Delta H^{\circ}) \qquad (13)$$

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* In the symmetry principle, the transition-state position is given by equation (A-1),[37,38] where E_a and ΔE are an activation energy and

$$n_T = E_a/(2\,E_a - \Delta E) \qquad \text{(A-1)}$$

reaction energy, respectively. Equation (13) can be derived by integrating equation (A-1) under the conditions of equation (A-2),

$$n_T = \alpha \equiv \mathrm{d}\,E_a/\mathrm{d}\,\Delta E \qquad \text{(A-2)}$$

which gives the definition of the Brönsted coefficient, α.

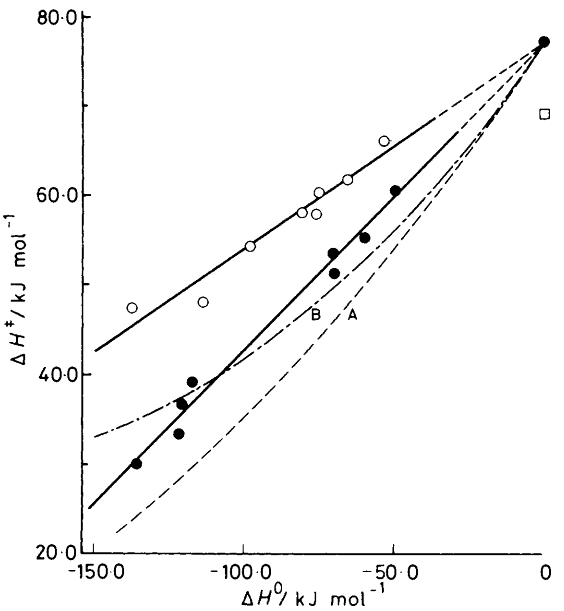

Figure 3. Correlations of activation enthalpies with reaction enthalpies for the reactions of various nucleophiles with methyl iodide in acetonitrile solvents. ○, Aromatic series; ●, aliphatic series; □, bromide ion.

A, Calculated with equation (10); B, calculated with equation (11), all with $\Delta H_0^{\ddagger}$ = 77.0 kJ mol^{-1}

which are applied to enthalpy change, and are shown in Figure 3 for comparison. Although the values calculated using the symmetry principle closely mimic the behaviour of the aliphatic series, the theoretical treatment cannot accommodate the experimental findings in two respects: firstly, theoretically the group that share common $\Delta H_0^{\ddagger}$ value are defined as a Brönsted series,[7,35] thus for the present case the presence of only one series is predicted for a group of neutral nucleophiles, although experimentally two series are observed; and secondly, theory predicts a slope of 0.5 in the region of ΔH° *ca.* 0; although each series seems to have a constant slope over the entire region covered by the experiments, 0.23 for the aromatic series and 0.34 for the aliphatic series, all are smaller than the theoretically predicted slope, 0.5.

To date, various types of extended Brönsted treatment have been carried out on Menschutkin-type reactions of methyl iodide. The coefficients of the plots are summarized in Table 6. These are all obtained with respect to the product pair of dissociated ions and not to the product ion pair. The second column of the Table summarizes the slopes of the plots shown in Figure 2, the third column summarizes the slopes of the activation enthalpy–reaction enthalpy correlation in terms of the change in physical interaction as a result of solvent variation in methanol + acetonitrile mixtures,[26,39] and the fourth column details the slope values in the plots in Figure 3.

In the previous section, the slope value of the extended Brönsted treatment in terms of volume correlation, 0.33, has been ascribed to the solvation change around the incipient iodide ion. Thermodynamic analysis of the slope values of activation enthalpy–reaction enthalpy correlation in terms of physical interaction, the third column in Table 6, has also led to the same conclusion.[26] The coefficient, 0.34, has also been obtained for the aliphatic series from activation enthalpy–reaction enthalpy correlations under the influence of variations of the nucleophile, the fourth column in Table 6. Thus, the coefficient, *ca.* 0.33, should be taken as the transition-state index, which has a particular bearing on the charge development of the incipient iodide ion. Coefficients other than *ca.* 0.33 in Table 6 suggest that the particular rate–equilibrium correlation is significantly affected by the specific nature of the relevant system.

Table 6. Coefficients of various extended Brönsted treatments

Nucleophile	$\Delta V_0^{\ddagger}$ *vs.* ΔV°	$\delta\ \Delta H^{\ddagger}_{\text{phys}}$ *vs.* $\delta\ \Delta H^{\circ}_{\text{phys}}$	$\Delta H^{\ddagger}$ *vs.* ΔH°
TPP	0.48		0.23
Pyridine	0.33[a]	0.38[b]	0.23
DMIT	0.33[a]	0.45[c]	0.34
TEA	0.09	0.35[b]	0.34

[a] Ref. 24. [b] Ref. 26. [c] Ref. 39.

With respect to the Menschutkin-type reactions, the early or late character of the changes in the three energy terms along the reaction co-ordinate is invoked as the major factor controlling the activation parameters for the reaction, *i.e.*, homolytic bond making and bond breaking, electronic reorganisation within the reacting molecule, and solvent reorientation around the reacting molecule. The analysis of solvent effects provides a very sensitive approach with respect to the degree of charge development along the reaction co-ordinate. The substrate effects, such as those shown in Figure 3, are the result of the three energy terms and thus provide an insensitive measure of the degree of charge development, compared with the solvent effects on reaction. However, the three thermodynamic parameters for the reaction, *i.e.*, reaction enthalpy, reaction entropy, and reaction volume, are all negative. In contrast, activation enthalpy has a positive value, while activation entropy and activation volume have negative values. This indicates that the direction of change of each constituent term of a particular thermodynamic quantity along the reaction co-ordinate is significant in determining the observed reaction co-ordinate profile. In other words, the difference in the relative proportions and in the response of inter- *versus* intra-molecular solvation to the developing charge would lead to the separation of neutral nucleophiles into two series.

The analysis of the constituents of the multiplicity of the extended Brönsted coefficients and the elaboration of the rate–equilibrium theory so as to incorporate the above multiplicities of Brönsted slopes might be a way forward.

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