The Reaction of *NN'*-Dimethylimidazolidine-2-thione and of 2,3-Dihydro-1,2,5-trimethyl-1,2,4-triazole-3-thione with Methyl Iodide. Reaction Rates, Transfer Enthalpies, and Extended Brönsted Treatments in Methanol–Acetonitrile Mixtures

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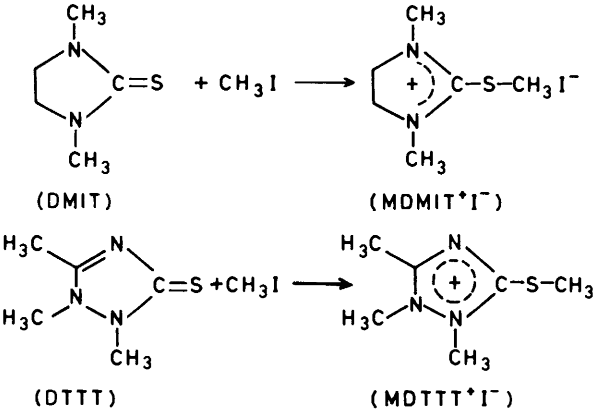
The rate constants and activation enthalpies for the reaction of two thione derivatives, *NN'*-dimethylimidazolidine-2-thione and 2,3-dihydro-1,2,5-trimethyl-1,2,4-triazole-3-thione, with methyl iodide have been measured in acetonitrile–methanol mixtures. Heats of solution were also measured for methyl iodide, two thione derivatives, and two methyl iodide salts of the thione in the same solvent mixtures. Some of the empirical energy correlations which have been carried out for the two reactions, one of the activation enthalpy *versus* activation free energy plots, and both the extended Brönsted relationships with respect to solvent variation exhibited non-linear behaviour. Transfer enthalpies of the above solutes have been rationalized in terms of ' more physical ' and of specific interactions. The extended Brönsted plots, which were performed in terms of ' more physical ' transfer enthalpies, exhibited linear patterns. The physical meaning of these plots is discussed.

Linear energy correlations such as those involving substituent, solvent, and temperature effects on reaction rates and equilibria have played a central role in mechanistic chemistry.[1-3] Theoretical conditions for the application of these correlations have been proposed from the thermodynamic and statistical mechanical points of view.[1-5]

The thermodynamic approach to understanding solvent effects on rates [6-8] and the more recent method for determining ion–molecule interactions in the gas phase [9-11] indicate clearly that for the observed quantities in solution such as activation and reaction parameters the constituent effects compensate for each other to different extents; thus the dissection of the parameters into these constituents is indispensable before a mechanical interpretation can be drawn from them. Sometimes the use of a mixed solvent instead of pure solvents is more convenient for dissecting the observed quantities into their constituents.[12-15]

In previous work anomalous solvent effects on the rates of the reaction of 2,3-dihydro-1,2,5-trimethyl-1,2,4-triazole-3-thione with methyl iodide have been noted, compared with the commonly observed trend for most thione–methyl iodide reactions.[16] In this work we report the rates and activation enthalpies for the 2,3-dihydro-1,2,5-trimethyl-1,2,4-triazole-3-thione (DTTT)–methyl iodide reaction, compared with those for the *NN'*-dimethylimidazolidine-2-thione (DMIT)–methyl iodide system, which is taken as the reference in methanol (MeOH)–acetonitrile (AN). We also report the enthalpy change of solution for reactants and products in the same solvent mixtures, and finally discuss the physical meaning of the extended Brönsted relationships in terms of a solvation model of the solutes.



Experimental

Materials.—*NN'*-Dimethylimidazolidine-2-thione, 2,3-dihydro-1,2,5-trimethyl-1,2,4-triazole-3-thione, and 1,3-dimethyl-2-methylthioimidazolidinium iodide were treated as described previously.[16] 2,3-*Dihydro*-1,2,5-*trimethyl*-3-*methylthio*-1,2,4-*triazolium iodide*, prepared by refluxing the corresponding thione derivative and methyl iodide in acetonitrile, was recrystallized three times from propan-2-ol and dried *in vacuo* over phosphorous pentaoxide at 65 °C (Found: C, 25.3; H, 4.25; N, 15.0. $C_6H_{12}IN_3S$ requires C, 25.25; H, 4.25; N, 14.75%). Solvents were purified as described elsewhere.[17,18]

Kinetics and Heats of Solution Measurements.—Kinetic measurements were performed as described elsewhere,[17,18] and activation enthalpies were deduced from the rate constants determined at four of the following temperatures: 0, 20.0, 30.0, 40.0, and 50.0 °C. Heats of solution were measured at 25.0 °C with a twin isothermal calorimeter (Tokyo Riko TIC-2D); the final concentrations used for measurements were *ca.* 2.3×10^{-2} for DMIT, 1.5×10^{-2} for DTTT, 1.2×10^{-2} for salts, and 1.5×10^{-1} mol dm^{-3} for methyl iodide. Experimental errors were estimated to be less than ±2%.

Results

Rate constants and activation parameters determined in methanol + acetonitrile mixtures are summarized in Table 1. As partly expected from the different rate behaviour in pure solvents (*cf.* Figure 3 of ref. 16), these measurements also indicate specific patterns in mixed solvents, *i.e.*, for the reaction of *NN'*-dimethylimidazolidine-2-thione with methyl iodide the log k_{mix} *versus* solvent composition profile gives a positive deviation from the line connecting the logarithmic rates in pure solvents, $x_1 \log k_1 + x_4 \log k_4$, while for the 2,3-dihydro-1,2,5-trimethyl-1,2,4-triazole-3-thione–methyl iodide

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

	DMIT-MeI		DTTT—MeI	
x_{MeOH}	10^4k_{mix} / dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger_{mix}$ / kJ mol^{-1}	10^3k_{mix} / dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger_{mix}$ / kJ mol^{-1}
1.0	1.72	70.4	5.98	62.2
0.8	3.07	66.4	11.1	
0.75			12.4	59.7
0.65	3.91	65.3	15.5	
0.5	4.65		21.0	58.4
0.35	5.52	62.6	29.7	
0.3			34.1	57.9
0.2	6.34	61.3	44.6	
0.1			65.4	55.1
0.0	7.67	60.5	114.0	51.3

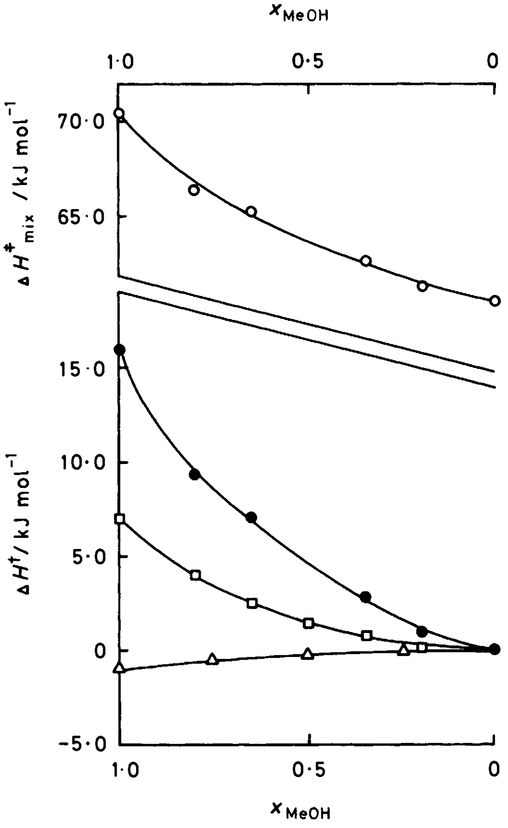


Figure 1. Activation enthalpy and transfer enthalpy *versus* solvent composition profiles in AN-MeOH mixtures for the DMIT-MeI reaction. ●, Activated complex; □, DMIT; △, MeI

reaction the profile gives a negative deviation. The contrasting behaviour of the two reactions is more clearly manifested in the activation enthalpy *versus* composition profile, as shown in the upper parts of Figures 1 and 2. For the latter (DTTT) reaction, the steeper change in activation enthalpies is noticeable at small methanol contents. Plots of activation enthalpy *versus* activation free energy constitute another way of appraising the contrasting rate behaviour, *i.e.*, for the DMIT reaction the slope, 2.60, leads to an isokinetic temperature of 496 K,[19,20] while for the DTTT reaction the plot is non-linear (see Figure 3).

Heats of solution are summarized in Table 2. Combination of these values with activation enthalpies enables the transfer enthalpies of the reactants and the activated complex to be deduced. These transfer values, with acetonitrile chosen as the reference solvent, are plotted against the mole fraction of methanol in the lower parts of Figures 1 and 2. For the DMIT reaction, the transfer enthalpies of both activated complex and thione steadily increase in value with increasing methanol content. The activated complex in the DTTT reaction shows a similar pattern of behaviour to that observed for the DMIT reaction. However, DTTT itself exhibits a shallow minimum, in contrast to the behaviour of DMIT. Thus, the main factor in the contrasting behaviour of the activation parameters is mostly reactant rather than transition state solvation.

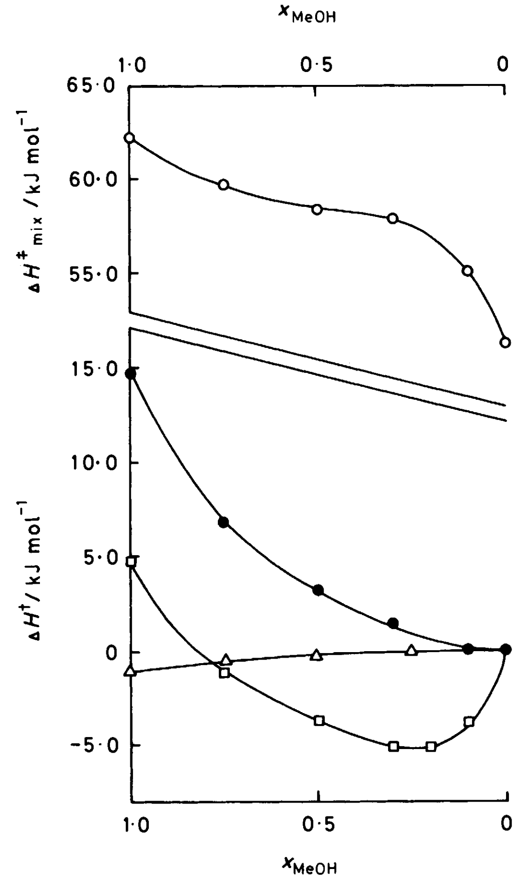


Figure 2. Activation enthalpy and transfer enthalpy *versus* solvent composition profiles in AN-MeOH mixtures for the DTTT-MeI reaction. ●, Activated complex; □, DTTT; △, MeI

Heats of solution have also been determined for both methyl iodide salts (Table 2). They exhibited a sharp minimum for small methanol contents, quite similar to the pattern observed for tetra-n-butylammonium bromide and iodide in the same solvent mixtures.[15] Because of the specificity in the transfer enthalpy patterns observed for the reactants, for the activated complexes, and for the products, the extended Brönsted plots with respect to solvent variation are far from linear, thus preventing a transition state index from being deduced from the plots (see Figure 4).

Discussion

With respect to the DMIT reaction, the transfer enthalpies of the reactants and activated complex show steady changes with respect to solvent composition. However, the minima ex-

Table 2. Enthalpy change of solution of the reactants and of the reaction products in acetonitrile–methanol mixtures (25.0 °C) (kJ mol^{-1})

x_{MeOH}	MeI	DMIT	MDMIT$^+$I$^-$	DTTT	MDTTT$^+$I$^-$
1.0	2.58	26.6	31.0	22.3	29.6
0.90					24.7
0.80		23.6	22.5		
0.75	3.08			16.4	19.7
0.65		22.1	18.8		
0.50	3.41	21.1	15.7	13.8	14.3
0.35		20.4	12.8		
0.30				12.4	10.7
0.25	3.59				
0.20		19.7	10.2	12.4	
0.10			9.45	13.7	8.41
0.0	3.62	19.6	12.8	17.5	11.9

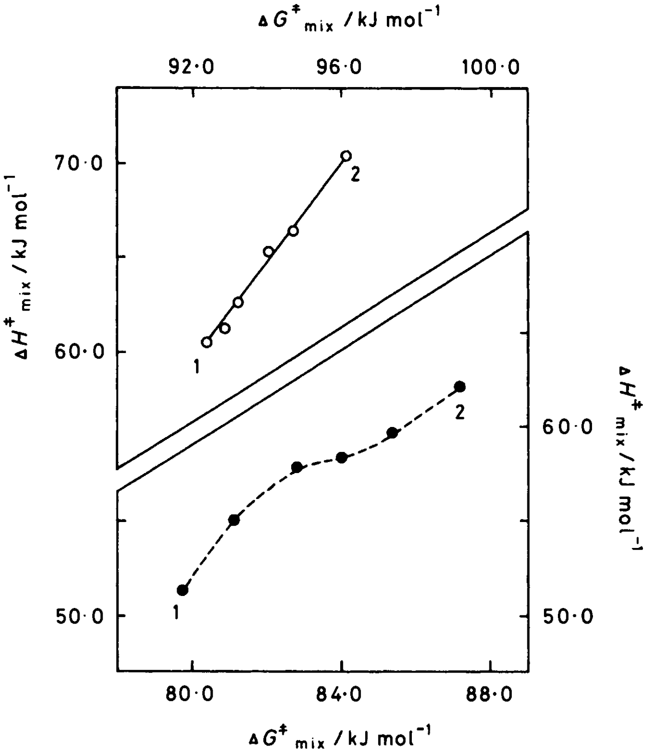


Figure 3. Plot of $\Delta H^{\ddagger}_{mix}$ against $\Delta G^{\ddagger}_{mix}$ in AN–MeOH mixtures at 30 °C. ○, DMIT–MeI reaction, slope 2.60, T_{hm}[19] 305.5 K; ●, DTTT–MeI reaction. 1, AN; 2, MeOH

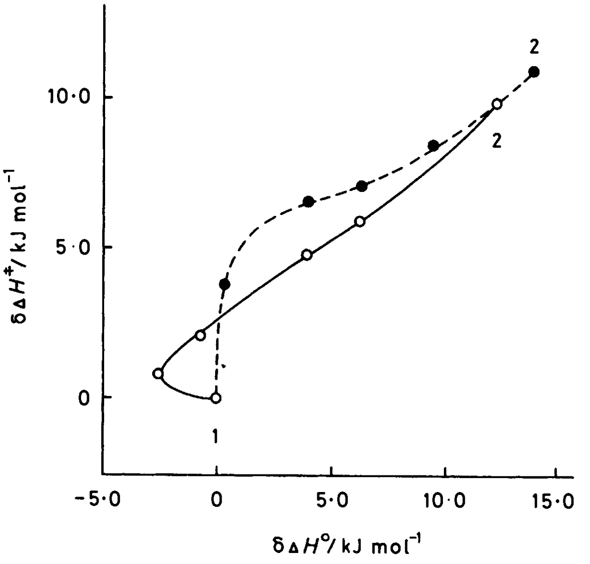


Figure 4. Extended Brönsted plots in AN–MeOH mixtures with respect to solvent variation. ○, DMIT–MeI reaction; ●, DTTT–MeI reaction. 1, AN; 2, MeOH

hibited in the transfer enthalpy *versus* solvent composition plots for DTTT and for the two salts is certainly a special feature that must be accounted for in terms of a molecular model before a full mechanistic interpretation can be given.

The specificity observed in the transfer enthalpy patterns for the two thione derivatives, *i.e.*, a steady change on the one hand, a minimum on the other, corresponds, in a sense, to the pattern observed previously for perchlorate and bromide ions in the same solvent mixtures.[14,15] Perchlorate ion shows a transfer enthalpy pattern quite similar to that of DMIT, while bromide and iodide ions exhibit a minimum.[14,15] These transfer enthalpies were rationalized by taking into account two types of interaction between a solute and solvents, *i.e.*, a ' more physical ' and a specific interaction.[14,15] The ' more physical ' interaction includes electrostatic interactions, van der Waals forces, solvent–structure modifying interactions, and cavity terms, *etc.*, while a specific interaction includes hydrogen bonding and charge-transfer interactions, *etc.*

The two thione derivatives have similar molecular sizes and structures to each other. Thus, it would not be unreasonable to assume that the transfer enthalpies arising from ' more physical ' interactions have the same functional dependence on the solvent composition for both thione derivatives, and the extra energy term which makes the behaviour of the triazole-3-thione derivative DTTT differ from the imidazolidine-2-thione derivative DMIT, arises from specific interaction between the former compound and methanol. The transfer enthalpy of *NN'*-dimethylimidazolidine-2-thione can be reproduced well by equation (1), where x stands for the

$$\Delta H_t^{AN\rightarrow mix} = \Delta H_t^{AN\rightarrow MeOH}\, x[1 - 1.2(1 - x)] \equiv \Delta H_{t,\,phys.}^{AN\rightarrow mix} \quad (1)$$

mole fraction of methanol. Thus, in the following treatment, we assume the above equation also applies to the transfer enthalpy of the triazole-3-thione derivative DTTT arising from ' more physical ' interaction.

Equations (2) and (3) have been derived and successfully used in rationalizing transfer enthalpies arising from specific interactions for bromide and iodide ions.[14,15] AS stands for an

Table 3. Dissection of transfer enthalpies into constituents in acetonitrile–methanol mixtures (25 °C) (kJ mol^{-1})

	DTTT		I^-	$MDMIT^+I^-$ *	$MDTTT^+I^-$ [a]
x_{MeOH}	$\Delta H_{t,\,SI}$	$\Delta H_{t,\,phys.}$	$\Delta H_{t,\,SI}$	$\Delta H_{t,\,phys.}$	$\Delta H_{t,\,phys.}$
1.0	−6.7	11.5	−10.0	28.2	27.7
0.90			−8.1		20.8
0.80			−7.2	16.9	
0.75	−6.5	5.4	−6.9		14.7
0.65			−6.4	12.4	
0.50	−6.2	2.3	−5.9	8.8	8.3
0.35			−5.65	5.6	
0.30	−5.6	0.55	−5.6		4.3
0.20	−5.0	0.1	−5.5	2.8	
0.10	−3.8	−0.1	−5.1	1.7	1.5
0.0	0.0	0.0	0.0	0.0	0.0

[a] Calculated as ΔH_t (salt) − $\Delta H_{t,\,SI}$ (I^-).

$$\Delta H_{t,\,SI}{}^{AS\rightarrow mix} = \Delta H_{t,\,SI}{}^{AS\rightarrow MeOH} K_{se}a_1/(K_{se}a_1 + a_4) \quad (2)$$

$$\Delta H_{t,\,SI}{}^{AS\rightarrow MeOH} = z\Delta H_{se} \quad (3)$$

aprotic solvent and a_i stands for the activity of solvent i assuming solvent exchange equilibria (4), and also a binomial distribution of clusters.

$$M\cdot(S_1)_{i-1}\cdot(S_4)_{z-i+1} + S_1 \underset{\Delta H_{se}}{\overset{K_{se}}{\rightleftharpoons}} M\cdot(S_1)_i\cdot(S_4)_{z-i} + S_4 \quad (4)$$

When mole fractions are used instead of activities in equation (2), then equation (5) holds.

$$\Delta H_{t,\,SI}{}^{AS\rightarrow mix} = \Delta H_{t,\,SI}{}^{AS\rightarrow MeOH} K_{se}x_1/(K_{se}x_1 + x_4) \quad (5)$$

Optimisation of transfer enthalpies has been carried out for the triazole-3-thione derivative DTTT, by using equations (1), (2), and (5) together with (6). By systematically changing the

$$\Delta H_t{}^{AN\rightarrow MeOH} = \Delta H_{t,\,SI}{}^{AN\rightarrow MeOH} + \Delta H_{t,\,phys.}{}^{AN\rightarrow MeOH} \quad (6)$$

values of $\Delta H_{t,\,SI}{}^{AN\rightarrow MeOH}$ and K_{se}, the optimum fit has been reached at $\Delta H_{t,\,SI}{}^{AN\rightarrow MeOH}$ −6.7 kJ mol^{-1}, and K_{se} 12.0, using equations (1) and (5). The calculated enthalpies are given in Table 3.

Previously, transfer enthalpies of iodide and bromide ions have been analysed in terms of ' more physical ' and specific interaction energies. With respect to iodide ion the optimum agreement has been obtained with $\Delta H_{t,\,SI}{}^{AN\rightarrow MeOH}$ −10.0 kJ mol^{-1}, and K_{se} 1.7 in acetonitrile–methanol.[15] Transfer enthalpies due to specific interactions of iodide ion can be calculated at any solvent composition, by substituting these parameters, and the activities of solvents as estimated before,[15] into equation (2). Combination of these values with the observed enthalpies for the salts enables the transfer enthalpies of the salts due to ' more physical ' interactions to be deduced (Table 3).

With respect to the two activated complexes, transfer enthalpies are quite close to each other, and no minimum, which would support the existence of a specific interaction between the activated complex and solvent, could be observed. Thus, it would not be unreasonable to assume that the transfer quantities are mostly composed of ' more physical ' interactions for the two activated complexes. The same view also applies to the transfer of DMIT and of methyl iodide.

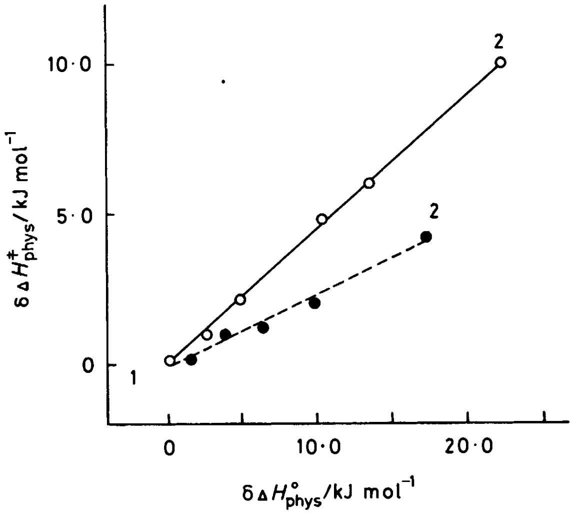


Figure 5. Extended Brönsted plots in terms of ' more physical ' interaction energies in AN–MeOH mixtures. ○, DMIT–MeI reaction, slope 0.45; ●, DTTT–MeI reaction, slope 0.25. 1, AN; 2, MeOH

Since the physical meaning of the transfer enthalpies has been made clear for all the solutes, it is now possible to carry out the extended Brönsted treatment in terms of the energy term which operates throughout reactants, activated complex, and products, that is, the ' more physical ' transfer enthalpy. As shown in Figure 5, both plots become linear, in marked contrast to those depicted in Figure 4, with the slopes falling in a reasonable range, 0.45 and 0.25 for DMIT–methyl iodide and for DTTT–methyl iodide, respectively.

The smaller coefficient for the DTTT–methyl iodide reaction might be taken as indicating that the transition state is earlier in this reaction than for the DMIT–methyl iodide reaction. However, transfer enthalpies of the activated complexes and of products behave quite similarly for both reactions, and this fact suggests that the transition states are comparable in terms of early or late character.

Transfer enthalpies from acetonitrile to methanol due to physical interactions are 7.0 (DMIT), 11.5 (DTTT), 15.9 (DMIT activated complex), 14.7 (DTTT activated complex), 28.2 (DMIT product), and 27.7 (DTTT product) in kJ mol^{-1}. These data indicate that the smaller coefficient for the DTTT–methyl iodide reaction does not mean the transition state lies early on the reaction co-ordinate compared to the DMIT–

methyl iodide reaction, but means the polarity of DTTT itself is greater than that of the DMIT.

Our treatment indicates that careful attention should be paid to the solvation of the solutes before mechanistic interpretations are drawn from empirical energy correlations.

Acknowledgements

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