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Reaction of 1-Ethyl-3-methyl-4-imidazoline-2-thione with Methyl Iodide. Kinetic and Thermodynamic Aspects

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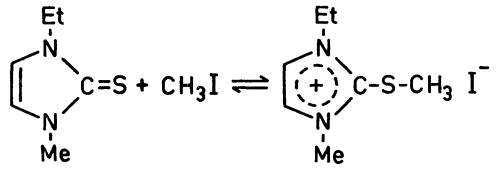
The reaction of 1-ethyl-3-methyl-4-imidazoline-2-thione with methyl iodide followed simple second order kinetics in polar solvents, whereas in less polar solvents the reverse process made a significant contribution to the overall rate. The solvent effects on the forward rate constant were linearly related to those on the rate of the reaction of tetramethylthiourea with methyl iodide. A plot of ΔV_0^* *vs.* $\Delta \overline{V}^\circ$ was linear with a slope of 0.33. From the volume changes and enthalpy changes measured, three transition state indices, $(\Delta_2 V^*/\Delta_2 \overline{V}^\circ)$, n_T and α were determined in acetonitrile, *ca.* 0.33, 0.32, and 0.41, respectively.

Much effort has recently been devoted to the rationalisation of solvent effects on kinetic and thermodynamic phenomena,[1-6] and it seems to have been commonly accepted that since the observed phenomena often result from combinations of various solvent characteristics, multiple parameter analysis is indispensable for such rationalisation. From another point of view, the relationships between kinetic and thermodynamic effects, especially those recently developed,[7-10] can be regarded as providing a theoretical basis for the characterisation of a solution reaction on terms of a transition state index.

As part of our continuing program to study any given process by as many different methods as possible, we analyse the reaction of 1-ethyl-3-methyl-4-imidazoline-2-thione (EMImdT) with methyl iodide which have a convenient rate,[11] from both kinetic and thermodynamic aspects, and then compare the results with those so far obtained for the reactions of the following thione derivatives with methyl iodide; 1,3-dimethyl imidazolidine-2-thione (DMIT),[12] *N,N,N',N'*-tetramethyl-thiourea (TMTU),[13] 3-isopropyl-4-methyl-4-thiazoline-2-thione (TT).[14]



Experimental

Materials. 1,3-Dimethyl-4-imidazoline-2-thione, prepared as described,[15] was recrystallized three times from benzene and was then dried over phosphorus pentaoxide. 1-Ethyl-3-methyl-4-imidazoline-2-thione, prepared from *N*-methylimidazole and ethyl iodide by the same procedure as described,[15] was recrystallized three times from ether–pentane mixture and was dried over phosphorus pentaoxide (Found: C, 50.54; H, 7.09; N, 19.61; S, 22.59%. Calcd for $C_6H_{10}N_2S$: C, 50.67; H, 7.09; N, 19.70; S, 22.54%). 1,3-Dimethyl-2-methylthioimidazolium iodide, prepared by refluxing the corresponding thione with methyl iodide in acetonitrile was recrystallized twice from methanol–ether mixture, and was dried *in vacuo* over phosphorus pentaoxide at 65 °C. (Found: C, 26.75; H, 4.12; N, 10.28%. Calcd for $C_6H_{11}IN_2S$: C, 26.68; H, 4.10; N, 10.37%). 1-Ethyl-3-methyl-2-methylthioimidazolium iodide, prepared by refluxing the corresponding thione and methyl iodide in ether, was recrystallized twice from methanol–ether mixture and was dried *in vacuo* over phosphorus pentaoxide at 65 °C (Found: C, 29.66; H, 4.62; N, 9.90%. Calcd for $C_7H_{13}IN_2S$: C, 29.59; H, 4.61; N, 9.86%).

Solvents were purified as described elsewhere.[14,16] Kinetic measurements and density measurements (at 2.5×10^{-2} mol dm^{-3}) were performed as described elsewhere.[14,16]

Heat of Reaction Measurements. The heat of reaction was measured at 25° C with a Tokyo Riko MPC-11 calorimeter used as a conduction type vessel. A methyl iodide solution (5.5×10^{-2} mol dm^{-3}) in acetonitrile or in propylene carbonate (25 cm^3) and 1-ethyl-3-methyl-4-imidazoline-2-thione solution (0.1165 g in 1.2 cm^3 of the respective solvent) sealed in an ampoule were placed in the calorimeter cell. After thermal equilibration, the ampoule was broken, with stirring, and the temperature was recorded on a chart over 20 h. Calibration was achieved by introducing a measured quantity of electrical energy. Two to three determinations yielded a heat of reaction ΔH_r in acetonitrile of -59.8 ± 2 (kJ mol^{-1}) and in propylene carbonate of -51.9 ± 0.8 (kJ mol^{-1}).

Heat of solution Measurements. Heats of solution were measured at 25.0 °C with a twin isothermal calorimeter (Tokyo Riko TIC-2D) at 1.2×10^{-2} mol dm^{-3} for salts, 2.5×10^{-2} mol dm^{-3} for thione derivatives, and 1.3×10^{-1} mol dm^{-3} for methyl iodide. The experimental error was estimated to be *ca.* 1% from duplicate or triplicate runs.

Results and Discussion

Rate Laws. In polar solvents the reaction of 1-ethyl-3-methyl-4-imidazoline-2-thione with methyl iodide followed second order kinetics as expected,[11,14] *i.e.*, first order in both EMImdT and methyl iodide. In cyclohexanone an equilibrium was eventually reached. In bromobenzene the precipitation of the produced salt started at the point marked by an arrow in Fig. 1. In benzene the salt precipitated from the beginning of the reaction and the reaction was treated by second order kinetics. For a comprehensive treatment of the kinetic data which were measured in homogeneous phase, the scheme was postulated, and data have been treated, as described elsewhere.[13,14] The subscript, *e*, denotes the concentration at equilibrium.

$$\underset{a-x}{\text{EMImdT}} + \underset{b-x}{\text{MeI}^-} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{x_{fi}}{\text{MEMImdT}^+} + \underset{x_{fi}}{\text{I}^-} \rightleftharpoons \underset{x_{ip}}{\text{MEMImdT}^+\text{I}^-}$$

$$2\,\underset{x_{ip}}{\text{MEMImdT}^+\text{I}^-} \rightleftharpoons \underset{x_q}{(\text{MEMImdT}^+\text{I}^-)_2}$$

Scheme 1.

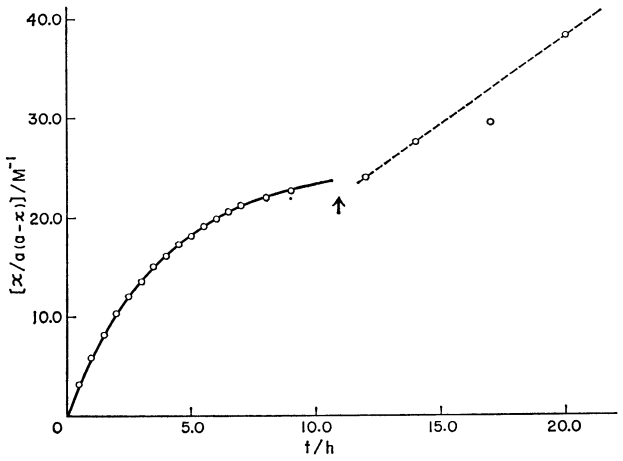


Fig. 1. Plots of $x/a(a-x)$ *vs.* t in bromobenzene at 30 °C.
○: Experimental, ——: calculated with $K_{obsd}=770$ $(dm^3mol^{-1})^{3/2}$ and $k_f=2.21\times10^{-3}$ $(dm^3\,mol^{-1}\,s^{-1})$. The arrow in the plots indicates the position where the precipitation of the salt started.

$$dx/dt = k_f(a-x)(b-x) - k_r x_{fi}^2 \quad (1)$$

$$K = k_f/k_r \quad (2)$$

$$K_{ip} = x_{ip}/x_{fi}^2 \quad (3)$$

$$K_q = x_q/x_{ip}^2 \quad (4)$$

$$x = x_{fi} + x_{ip} + 2x_q$$
$$= x_{fi} + K_{ip}x_{fi}^2 + 2K_qK_{ip}^2x_{fi}^4 \quad (5)$$

$$k_f(a-x_e)(b-x_e) = k_r x_{fi,e}^2 \quad (6)$$

In cyclohexanone the stoichiometric equilibrium constant, K_{sto}, determined analytically is rearranged to Eq. 8. From the set of x_e and K_{sto} values the equations were solved simultaneously to give $K=0.274$, $K_{ip}=1.25\times10^3$ dm³ mol⁻¹, $K_q=8.84$ dm³ mol⁻¹ (Fig. 2). The forward rate constant, k_f was calculated from Eq. 9 by the procedure described.[13,14]

$$K_{sto} = x_e^2/\{(a-x_e)(b-x_e)\} \quad (7)$$

$$(K_{sto}/K)^{1/2}$$
$$= 1 + K_{ip}(Kx_e^2/K_{sto})^{1/2} + 2K_qK_{ip}^2(Kx_e^2/K_{sto})^{3/2} \quad (8)$$

$$\int_0^x \frac{dx}{(a-x)(b-x)-x_{fi}^2/K} = \int_0^t k_f dt \quad (9)$$

In bromobenzene the assumption, $x_q \gg x_{fi}$ and x_{ip} seems plausible[12,13] and under the conditions the observed equilibrium constant as defined by the left hand side of Eq. 10 leads to the right hand side of Eq. 10. The forward rate constant, k_f was obtained

$$K_{obsd} \equiv x_e^{1/2}/[(a-x_e)(b-x_e)] = K(2K_qK_{ip}^2)^{1/2} \quad (10)$$

by performing the integration as described,[13,14] and the comparison of the experimental sets of x *vs.* t data

$$\int_0^x \frac{dx}{(a-x)(b-x)-K_{obsd}^{-1}x^{1/2}} = \int_0^t k_f dt \quad (11)$$

with the theoretical values calculated on the basis of the Scheme indicates fair agreement (Fig. 1). The kinetically determined equilibrium constant, $K_{obsd}=770$ $(dm^3\,mol^{-1})^{3/2}$ is in a comparable range with those observed previously (18.0—4400 $(dm^3\,mol^{-1})^{3/2}$),[12-14] though the value could not be verified analytically because of the precipitation of the produced salt.

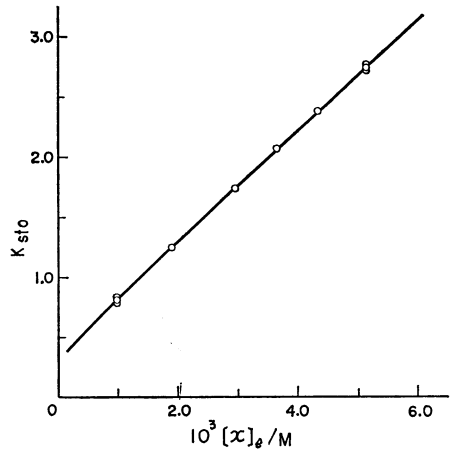


Fig. 2. Plots of K_{sto} *vs.* x_e at 30 °C.
○: Experimental, ——: calculated with $K=0.274$, $K_{ip}=1.25\times10^3$ $(dm^3\,mol^{-1})$ and $K_q=8.84$ $(dm^3\,mol^{-1})$.

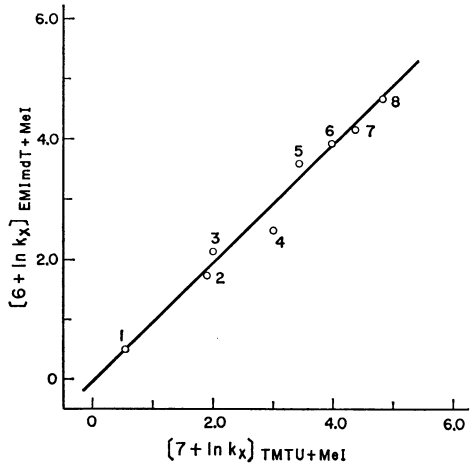


Fig. 3. Empirical correlations for rate constants.
○: Experimental, 1: benzene, 2: 2-propanol, 3: bromobenzene, 4: methanol, 5: cyclohexanone, 6: nitrobenzene, 7: acetonitrile, 8: propylene carbonate.

TABLE 1. RATE CONSTANTS FOR THE REACTION OF 1-ETHYL-3-METHYL-4-IMIDAZOLINE-2-THIONE WITH METHYL IODIDE (30 °C)

Solvents	$10^3\,k_f/dm^3\,mol^{-1}\,s^{-1}$	$10^2\,k_x/s^{-1}$
Propylene carbonate	22.3	26.1
Acetonitrile	8.36	15.7
N,*N*-Dimethylacetamide	12.9	13.8
Nitrobenzene	12.8	12.4
Cyclohexanone	9.25	8.83
Bromobenzene	2.21	2.08
Benzene	0.366	0.407
Methanol	1.21	2.96
2-Propanol	1.08	1.39

Table 2. Comparison of the kinetic and thermodynamic data (30 °C)

Reactions	$10^3 k_f$[a] / dm^3 mol^{-1} s^{-1}	K[a]	Slope[b]	ΔH^*[c] / kJ mol^{-1}	ΔH_r[c,d] / kJ mol^{-1}
EMImdT+MeI	9.25	0.274	0.97	55.2	−59.8
TMTU+MeI[13]	2.93	0.231	1.0	53.5	−70.3
DMIT+MeI[12]	0.721	1.35×10^{-3}	0.79	60.7	−49.8
TT+MeI[14]	0.640	1.08×10^{-2}	0.77	—	—

a) In cyclohexanone. b) Slope of Fig. 3 type correlation. c) In acetonitrile. d) At 25 °C.

Table 3. Apparent molal volumes, ϕ_v, the overall volume change of reaction, $\Delta\phi_v$, and activation volumes, ΔV_0^*, and their pressure derivatives (30 °C)

Solvents	ϕ_v/cm^3 mol^{-1}			$\Delta\phi_v$ / cm^3 mol^{-1}	ΔV_0^* / cm^3 mol^{-1}	$(\partial\Delta V^*/\partial p)_0$ / cm^5 mol^{-1} N^{-1}
	EMImdT	MeI	MEMImdT$^+$I$^-$			
Acetonitrile	124.6	67.1	151.4	−40.3	−21.8	7.25×10^{-4}
Propylene carbonate	131.1	65.1	174.3	−21.9	−16.4	4.60×10^{-4}
N,N-Dimethylacetamide	127.0	64.7	161.0	−30.7	−16.7	5.35×10^{-4}
Acetonitrile	106.4[a]	67.1	133.6[b]	−39.9		

a) DMImdT. b) MDMImdT$^+$I$^-$.

Solvent Effects on the Rate Constants, k_f. The rate constants, k_f for the present reaction are summarized in Table 1, where k_x values calculated from the rate constant, k_f, and the molar volume of the solvent, V_s, expressed in dm^3 mol^{-1} by the equation, $k_x = k_f V_s^{-1}$ are also given.

There is a linear free energy relationship between the values of $\log k_x$ for the present reaction and the reaction of *N,N,N',N'*-tetramethylthiourea with methyl iodide. (Fig. 3). The slope is 0.97.

In Table 2, typical values of the kinetic and thermodynamic data are summarized for comparison, where the reaction of TMTU with methyl iodide is taken as a standard reaction for comparison of the solvent effect.

The solvent effects on the rates of these ion forming reactions have been taken as giving the measure of the position of the transition state along the reaction coordinate, and were sometimes invoked as criteria for or against the operation of the reactivity-selectivity principles.[7-10] As far as these reactions are concerned, the first two reactions which proceed faster, have a larger sensitivity to solvent changes. In contrast to this observation, with respect to structural variations there seems to be some kind of correlation between kinetic and thermodynamic quantities, *i.e.*, a larger rate constant accompanies a larger equilibrium constant, and the activation enthalpy decreases with decreasing reaction enthalpy. Considering these trends, the interpretation of solvent effects on kinetics and thermodynamics needs deeper insights into the molecular processes operating in solution.

Activation Volumes and Volume Changes of Reaction. Activation volumes, ΔV_0^* and their pressure derivatives were determined by the least-squares method after expanding the rate constant into a power series of the pressure, Eqs. 12—14.

$$\ln k_p = \ln k_0 + Bp + Cp^2 \quad (12)$$

$$\Delta V_0^* = -1\ BRT \quad (13)$$

$$(\partial\Delta V^*/\partial p)_0 = -2\ CRT \quad (14)$$

The apparent molal volumes of the solutes, ϕ_v and the overall volume change in the reaction, $\Delta\phi_v$ are summarized in Table 3.

The volume behavior observed for the present reaction confirms the trends mentioned previously,[12] first, that molal volumes of thione derivatives and of ionic products are always larger in propylene carbonate than in acetonitrile and second, that the reaction in acetonitrile gives larger negative volume changes than in propylene carbonate, on activation as well as on reaction.

Recently, on the basis of the X-ray structural analysis[17] a polar structure with a partial negative charge on sulfur atom has been postulated for 1,3-dimethyl-4-imidazoline-2-thione. The apparent molal volume has also been measured for the compound for comparison. The molal volume difference of 7.7 cm^3 mol^{-1} between 1,3-dimethyl-4-imidazoline-2-thione (DMImdT) and 1,3-dimethylimidazolidine-2-thione (114.1 cm^3 mol^{-1} in acetonitrile[12]) would largely be ascribed to the molal volumes of two hydrogen atoms bonded to the ethylenic linkage of dimethylimidazolidine-2-thione. The estimation developed by Edwards and Bondi which relates the molal volumes to van der Waals volumes and surface areas,[18,19] gives 6.7 cm^3 mol^{-1} for the difference and this supports the above views. The methylene group contribution as deduced from molal volumes of two thione derivatives EMImdT and DMImdT, 18.2 cm^3 mol^{-1} agrees also with their estimation.[19] Thus, at this point, it is indeterminable to what extent the polarity of the solute manifests itself on the molal volume determined in dilute solution.

A fairly nice linear relationship, Eq. 15 exists be-

TABLE 4. ENTHALPY CHANGE OF SOLUTION, ΔH_s, AND OF REACTION, ΔH_r, AND ACTIVATION ENTHALPIES, ΔH^*

Solvents	ΔH_s/kJ mol^{-1} (25.0 °C)			ΔH_r / kJ mol^{-1}	ΔH^* / kJ mol^{-1}
	EMImdT	MeI	MEMImdT+I$^-$		
Propylene carbonate	17.7	3.30	26.4	−51.9	53.5
Acetonitrile	17.5	3.64	21.2	−59.8	55.2
N,*N*-Dimethylacetamide	12.3	0.23	15.9	—	55.6
Methanol	22.0	2.59	38.4	—	—
N,*N*-Dimethylacetamide	17.8[a]	0.23	11.7[b]		
Methanol	26.6[a]	2.59	31.0[b]		

a) DMIT. b) MDMIT+I$^-$.

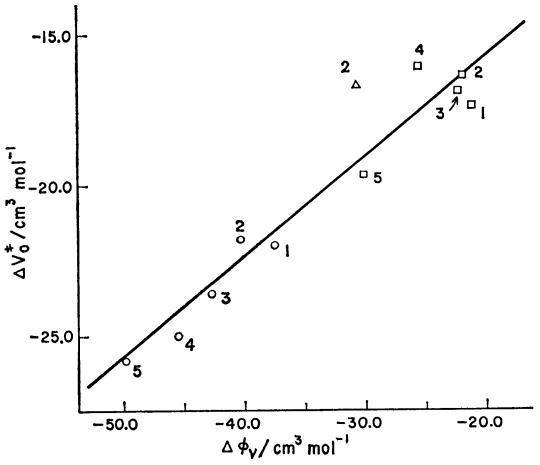


Fig. 4. Plots of ΔV_0^* *vs.* $\Delta\phi_v$.
Solvents: ○: acetonitrile, □: propylene carbonate, △: *N*,*N*-dimethylacetamide. Reactions: 1: TMTU+MeI, 2: EMImdT+MeI, 3: DMIT+MeI, 4: TT+MeI, 5: pyridine+MeI.

tween activation volumes and the overall volume changes of reactions studied by the authors, surprisingly including pyridine—methyl iodide reaction (Fig. 4). However, the possibility should be kept in mind

$$\Delta V_0^* = 0.33\Delta\phi_v - 9.2/\text{cm}^3\,\text{mol}^{-1} \quad (15)$$

that the linear relationship might be an artifact, since the points determined in propylene carbonate suggest a different trend from that obtained from the data in acetonitrile, though the regression line passes through the averaged point; also the point in dimethylacetamide largely deviates from the regression line. In the same vein as proposed previously,[12,13] the slope can be equated to the charge development index at the transition state, and the Eq. 16 can be derived,

$$\frac{\Delta V_0^* - \Delta_1 V^*}{\Delta\overline{V}^\circ - \Delta_1\overline{V}^\circ} = 0.33 \quad (16)$$

where the suffix, 1 indicates the structural volume changes on activation as well as on reaction. The combination of Eqs. 15 and 16 yields Eq. 17. In

$$\Delta_1 V^* - 0.33\Delta_1\overline{V}^\circ = -9.2/\text{cm}^3\,\text{mol}^{-1} \quad (17)$$

these derivations the apparent molal volumes were equated to the partial molal volumes ($\Delta\phi_v = \Delta\overline{V}^\circ$), taking into account the experimental conditions.

The structural volume changes have been estimated on various grounds, that is, for $\Delta_1 V^*$ they range from −6.5 to −11.7 cm^3 mol^{-1} [13,20–22] and for $\Delta_1\overline{V}^\circ$ from −4 to 0 cm^3 mol^{-1}.[13,14,20] Equation 17 does not give any preference to the respective set of values but serves as the criteria for the consistency of a given estimation. Considering these estimated values and also the relation (17), the set of central values, presumably the most plausible values, are taken as −10.1 and −2.8 cm^3 mol^{-1} for $\Delta_1\overline{V}^*$ and $\Delta_1 V^\circ$. The derived value, −10.1 cm^3 mol^{-1} for $\Delta_1 V^*$ is in fair agreement with the value, −10.7 cm^3 mol^{-1} estimated on completely different grounds.[21]

Enthalpy Measurements. Various enthalpies are summarized in Table 4. Throughout the two series of reactions, *i.e.*, DMIT with methyl iodide[12] and EMImdT with methyl iodide, the activation enthalpy has larger values in acetonitrile than in propylene carbonate, while the reaction enthalpy has larger negative values in acetonitrile than in propylene carbonate. With respect to structural variations there is observed some kind of relation between kinetics and thermodynamics as expected from the reactivity—selectivity pattern. In this regard also, the interpretation of the solvent effects on rates needs deeper insights. As a candidate, at least the cavity effect[23–25] would have to be invoked, though its' evaluation seems to present various problems.[23–25] On activation, as well as on reaction, reactants lose their volumes, *i.e.*, $\Delta_1 V^*$ and $\Delta_1\overline{V}^\circ$, and the work required to make a cavity in solution would differently affect activation enthalpies and reaction enthalpies. For rationalizing solvent effects on rates and on equilibria these would have to be evaluated on some basis. Abraham's way of taking an ion-pair as a final product[26] would provide one method for avoiding the complexity due to the cavity effect.

The thione derivatives as well as their methyl iodide salts give rise to characteristic transfer enthalpies. This might be ascribed to the polarity difference between the two thione derivatives DMIT and EMImdT, which could not be detected by the molal volume measurements. However, because of cancellations between reactants and products, a linear relation holds between the transfer reaction enthalpies, enthalpies of transfer from acetonitrile to other solvents of reaction, $\Delta H_{r,t} = \Delta H_{r,S} - \Delta H_{r,AN}$, of the two series (Fig. 5), and the slope of the plot, 0.86 is quite close to the ratio of the slopes of the linear free energy relationships

Table 5. Transition state indices for the reaction of 1-ethyl-3-methyl-4-imidazoline-2-thione with methyl iodide (30 °C)

Solvents	Slope	n_T	α
Acetonitrile	0.33	0.32	0.41
Propylene carbonate	0.33	0.34	0.42

as mentioned above, *i.e.*, (0.79/0.97)=0.82. This suggests that with respect to solvent variations, some sort of relation is operating between kinetics and thermodynamics as inferred from reactivity—selectivity pattern, though its direct proof would require much more effort.

Transition State Indices. Three kinds of transition state indices are compared in Table 5. The first is the charge development parameter which is defined as the slope of the plot of ΔV_0^* *vs.* $\Delta\overline{V}^\circ$. The second index has been calculated from the equation,

$$n_T = \frac{E_a}{(2E_a - \Delta E)} \tag{18}$$

where E_a and ΔE stand for the activation energy and the enthalpy change of the reaction.[8,9] The third index has been calculated by applying Marcus equations following the procedure as described by Albery and Kreevoy.[27,28] In the latter two calculations the activation enthalpy and the enthalpy change of the reaction have been directly substituted into these equations. Thus, judging from the experimental conditions, these indices would refer to the dissociated pair of ions as the final state.

$$\Delta G^* = \Delta G_0^* + (1/2)\Delta G^\circ + \Delta G^{\circ 2}/16\Delta G_0^* \tag{19}$$

$$\alpha = (1/2)(1+\Delta G^\circ/4\Delta G_0^*) \tag{20}$$

Recently Arnett *et al.*,[29] performed a complete kinetic and thermodynamic dissection of alkyl transfers. The Brönsted type plots gave linear relations and the slopes amount to 0.26 for the free energy correlation and to 0.23 for enthalpy correlation. On the other hand, the direct substitution of their enthalpies into Eq. 18, and Eqs. 19 and 20, and averaging afterwards lead to 0.30 and 0.39 for n_T and α. On the other hand Albery[30] calculated α ranging from 0.45 to 0.49 on the basis of the activation free energies and reaction free energies determined by Arnett *et al.*[29] Theoretical considerations demand the coincidence between the slope of the Brönsted type plots and the direct theoretical calculations as performed above.[10] In this regard for the Menschutkin reactions, n_T values indicate rather self-consistency. A similar situation holds for the present case, since n_T values obtained for the present reaction as well as for the previous reactions,[12-14] indicate close proximity to the charge development parameter as obtained from the volume correlation.

Here, again it should be pointed out that so far as we are concerned with a structurally related series of compounds, for a volume change correlation such as Fig. 4, structural volume changes, $\Delta_1 V^*$ and $\Delta_1\overline{V}^\circ$, could reasonably be assumed to be constant over the series. In contrast, for regular Brönsted type correlations such as ΔH^* *vs.* ΔH° or ΔG^* *vs.* ΔG°, the slope consists of two contributions, *i.e.*, a structural term and a solvational term accompanying structural variations. Thus the dissection of the slope into its constituent terms would be desirable for a more consistent comparison of the two types of slopes.

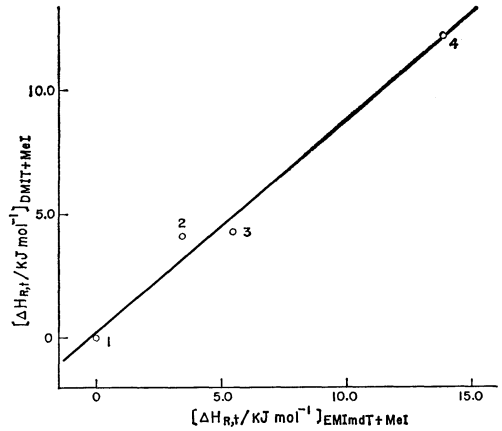


Fig. 5. Empirical correlations for the transfer reaction enthalpies (25 °C).
1: Acetonitrile, 2: *N,N*-dimethylacetamide, 3: propylene carbonate, 4: methanol.

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