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The Reaction of 4-Thiazoline-2-thione with Methyl Iodide. Solvent Effects and Pressure Effects

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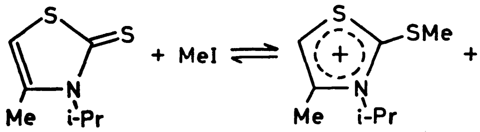
Rate constants for the reaction of 3-isopropyl-4-methyl-4-thiazoline-2-thione with methyl iodide have been determined in several solvents at 1 atm. In acetonitrile and propylene carbonate, the reaction was studied at pressures up to 1500 atm by a conductivity method. A comparison of the activation volume and overall volume change of reaction, obtained from density measurements, suggests that the charge development at the transition state is only fractional. The results of CNDO/2 calculations support the argument.

In a previous paper[1)] we called attention to the correlation of the solvent effect on reaction rates and activation volumes for a series of Menschutkin reactions. In particular, it was shown that the reaction in which the rate has a larger sensitivity to solvent characteristics exhibits a greater solvent effect on the activation volumes.

With the aim of determining the range of applicability of such correlations on reactions of the same charge type, we examined the solvent and pressure effects on the reaction of 3-isopropyl-4-methyl-4-thiazoline-2-thione (TT) with methyl iodide, since it is of the same charge type as the Menschutkin reaction[2)] but with a different nucleophilic center. The results are given in this report.



(TT)　　(MTT⁺ + I⁻)

Experimental

Materials. Propylene carbonate (Wako EP grade) was dried over freshly activated molecular sieves and distilled three times under reduced pressure. The other solvents (Wako guaranteed grade) were purified.[1,3)] 3-Isopropyl-4-methyl-4-thiazoline-2-thione (TT)[2,4,5)] was recrystallized three times from aqueous ethanol and dried *in vacuo* at 65 °C before use. [Found: H, 6.39; C, 48.29; N, 8.09%. Calcd for $C_7H_{11}NS_2$: C, 48.51; H, 6.40; N, 8.08%]

2-Methylthio-3-isopropyl-4-methylthiazolium iodide ($MTT^+ I^-$), prepared by refluxing TT and methyl iodide, was recrystallized three times from *N*,*N*-dimethylacetamide–ether mixture and dried *in vacuo* at 65 °C before use. [Found; I, 40.14%, Calcd for $C_8H_{14}INS_2$: I, 40.26%] *N*-Methylpyridinium iodide, prepared from pyridine and methyl iodide, was recrystallized three times from *N*,*N*-dimethylacetamide–ether mixture and dried *in vacuo* at 65 °C before use. [Found; I, 57.06%, Calcd for C_6H_8IN: I, 57.41%]

Kinetic Measurements. Equal volumes of a halide solution and a TT solution (*ca.* 0.01 M), or pyridine solution (*ca.* 0.01 M) were mixed rapidly in a stoppered flask, aliquots of the reaction mixture being withdrawn at intervals and titrated potentiometrically with a siver nitrate solution.[1)] In acetonitrile and propylene carbonate, the rates were determined conductimetrically in glass cells immersed in the pressure vessel. The conductivity cell, capacity *ca.* 15 ml, was equipped with platinum electrodes (1 cm × 1 cm, 1 cm apart). Since no direct proportionality between conductance and ion concentration was observed in these solvents, the dependence of conductance on concentration, not corrected for solvent compression, was dermined for methylpyridinium iodide and MTT^+I^- solutions in both solvents under pressure (1, 300, 600, 900, 1200 and 1500 kg cm^{-2}) at 30 °C. Calculation of the rate constant was carried out after transforming the measured resistance into the concentration at atmospheric pressure. The activation volumes thus calculated should be taken as expressed in mole fraction unit. A few runs at atmospheric pressure were followed by titration of halide ion. The rate constants determined by these methods agreed within experimental error. The errors were estimated to be less than ±2% from duplicate or triplicate runs.

Density Measurements. The densities of the solution were measured in a glass dilatometer calibrated with doubly distilled water, having a bulb of *ca.* 40 ml capacity and two graduated stems. The apparent molal volumes were calculated by the equation

$$\phi_v = \frac{1000(d_0-d)}{cd_0} + \frac{M_2}{d_0} \tag{1}$$

where the quantities have their usual meaning. The concentration of the solute was 0.01—0.02 M except for methyl iodide and pyridine for which it was 0.1—0.2 M. The errors were estimated to be less than ±0.4 cm^3 mol^{-1} from duplicate or triplicate runs.

Results and Discussion

Rate Law. A characteristic feature of the reaction of TT with methyl iodide is that the rate law changes according to the polarity of the solvent, since in low or medium dielectric solvents the reverse process has an effect on the observed rate.

In dipolar solvents such as acetonitrile (AN), propylene carbonate (PC), methanol, *N*,*N*-dimethylacetamide, and nitrobenzene, the rate law followed second order kinetics as expected, *i.e.*, first order in TT and in methyl iodide.

In cyclohexanone and bromobenzene the rate behavior was rather complicated, probably because of ion-pair and various kinds of higher aggregates formed in these solvents.[6,7)]

For a comprehensive treatment of these two cases the following reaction schemes were postulated.

$$\begin{array}{ccccccc} TT & + & MeI & \underset{k_r}{\overset{k_f}{\rightleftarrows}} & MTT^+ + I^- & \rightleftarrows & MTT^+\,I^- \\ a-x & & b-x & & x_{fi} \quad\; x_{fi} & & x_{ip} \end{array}$$

$$\begin{array}{ccc} 2MTT^+\,I^- & \rightleftarrows & (MTT^+\,I^-)_2 \\ x_{ip} & & x_q \end{array}$$

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_f(a-x)(b-x) - k_r x_{fi}^2 \tag{2}$$

$$K = (k_f/k_r) \tag{3}$$

$$K_{ip} = x_{ip}/(x_{fi})^2 \tag{4}$$

$$K_q = x_q/(x_{ip})^2 \tag{5}$$

$$\begin{aligned} x &= x_{fi} + x_{ip} + 2x_q \\ &= x_{fi} + K_{ip}x_{fi}^2 + 2K_qK_{ip}^2x_{fi}^4 \end{aligned} \tag{6}$$

At equilibrium the following equation holds,

$$k_f(a-x_e)(b-x_e) = k_r x_{fi'e}^2 \tag{7}$$

where the suffix, e, denotes the concentration at equilibrium.

In cyclohexanone the observed equilibrium constant, K_{obsd}, is defined by the equation

$$K_{obsd} = x_e{}^2/\{(a-x_e)(b-x_e)\}. \tag{8}$$

This is transformed into the following equation by combining Eqs. 3, 6, 7, and 8:

$$\begin{aligned} K_{obsd} &= K(x_e{}^2/x_{fi'e}^2) \\ &= K(1+K_{ip}x_{fi'e}+2K_qK_{ip}^2x_{fi'e}^3)^2 \end{aligned} \tag{9}$$

By rearranging we have,

$$\begin{aligned} (K_{obsd}/K)^{1/2} &= 1 + K_{ip}(Kx_e{}^2/K_{obsd})^{1/2} \\ &\quad + 2K_qK_{ip}^2(Kx_e{}^2/K_{obsd})^{3/2} \end{aligned} \tag{10}$$

The values of K_{obsd}, determined analytically after keeping the reaction mixtures at 30 °C for a sufficiently long time (usually for a week), and the corresponding values of x_e were substituted into Eq. 10. Several such equations were solved simultaneously to give $K=1.08\times 10^{-2}$, $K_{ip}=1.11\times 10^3$ M^{-1}, and $K_q=3.35$ M^{-1}.

The calculated values of K_{obsd} (on the basis of the above set of equilibrium constants) as a function of x_e are compared with the experimental values (Fig. 1).

The values of K_{ip} thus determined (1.11×10^3) seem to be in the correct order of magnitude, since the association constants of quaternary ammonium halides in methyl ethyl ketone which has a dielectric constant comparable with that of cyclohexanone, are in the range 400—1000 M^{-1}.[8)]

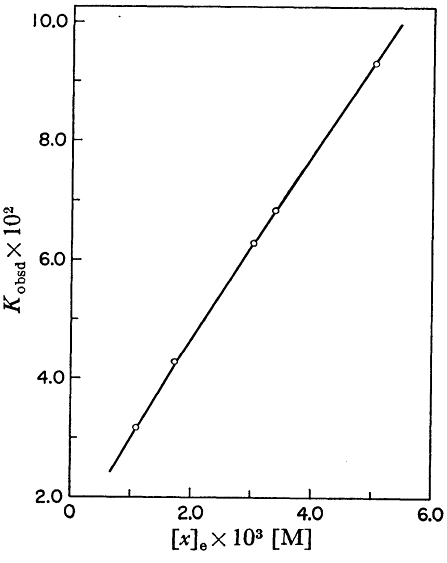


Fig. 1. Plots of K_{obsd} *vs.* $(x)_e$ at 30 °C.
○; Experimental, —; calculated with $K=1.08\times 10^{-2}$, $K_{ip}=1.11\times 10^3$(M^{-1}), $K_q=3.35$(M^{-1}).

The values of x_{fi} at a given time were obtained by solving the biquadratic equation 6 with respect to x_{fi} by the Newton-Raphson method for the measured values of x.

The integration of Eq. 11 was carried out after expanding the integrand into a power series of x as given by Eq. 12.

$$\int_0^x \frac{\mathrm{d}x}{(a-x)(b-x)-x_{fi}^2/K} = \int_0^t k_f\mathrm{d}t \tag{11}$$

$$\frac{1}{(a-x)(b-x)-x_{fi}^2/K} = \frac{1}{ab} + Bx + Cx^2 + Dx^3 \tag{12}$$

The forward rate constants thus obtained showed no systematic deviation from the average value over three fold changes of initial concentration of the reactants.

In bromobenzene, the assumption $x_q \gg x_{fi}$ and x_{ip} seems plausible, and leads to a simplified rate law.

$$x \approx 2x_q = 2K_qK_{ip}^2x_{fi}^4 \tag{13}$$

$$\therefore \quad x_{fi} = (x/2K_qK_{ip}^2)^{1/4} \tag{14}$$

If we denote the observed equilibrium constant by K_{obsd}, we have the following relation from a combination of Eqs. 3, 7, and 14.

$$\begin{aligned} K_{obsd} &= k_e{}^{1/2}/\{(a-x_e)(b-x_e)\} \\ &= K(2K_qK_{ip}^2)^{1/2} \end{aligned} \tag{15}$$

Under these conditions Eq. 2 is reduced to

$$\frac{\mathrm{d}x}{\mathrm{d}t} = x_f\{(a-x)(b-x)-K_{obsd}^{-1}x^{1/2}\}. \tag{16}$$

$$\int_0^x \frac{\mathrm{d}x}{(a-x)(b-x)-K_{obsd}^{-1}x^{1/2}} = \int_0^t k_f\mathrm{d}t \tag{17}$$

On the basis of Simposon's rule, graphical integrations were repeated for the assumed values of k_f and K_{obsd}, until the calculated set of x *vs.* t data agreed with the experimental values. The best sets for K_{obsd} and k_f were 47.5 M$^{-1/2}$, and 2.97×10^{-4} M^{-1} s^{-1}, respectively.

The equilibrium constant determined kinetically (47.5

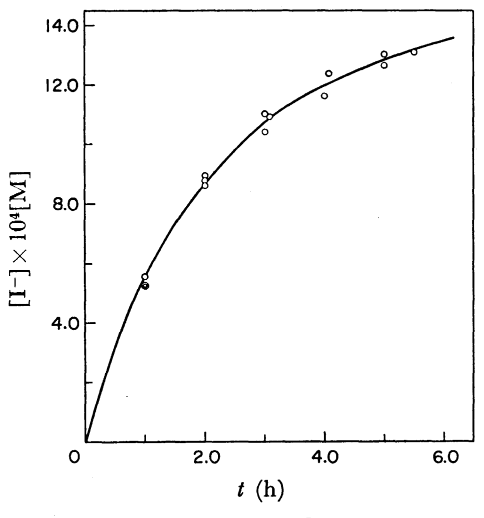


Fig. 2. Plots of (I$^-$) *vs.* t at 30 °C.
○; Experimental, —; calculated with $K_{obsd}=47.5$ (M$^{-1/2}$), $k_f=2.97\times 10^{-4}$ (l mol^{-1} s^{-1}), $a=b=3.00\times 10^{-2}$ (M).

$M^{-1/2}$) was in good agreement with the value determined analytically (46.5 $M^{-1/2}$). A comparison of the calculated values of x with the experimental ones is shown in Figure 2.

The values of k_f and K_{obsd} were also determined by direct differentiation of x with respect to t after expanding x into a power series of t as in $x=at+bt^2+ct^3$, followed by calculation of the value of K_{obsd} which gave a constant value of k_f throughout the run. The values determined by the two methods were in good agreement.

Solvent Effects on the Rate Constant, k_f. The rate constants, k_f, are summarized in Table 1, where k_x denotes the rate constant expressed in mole fraction unit as calculated from the rate constant, k_f, and the molar volume of the solvent, V_s, (expressed in liter) by the equation, $k_x=k_f V_s^{-1}$.

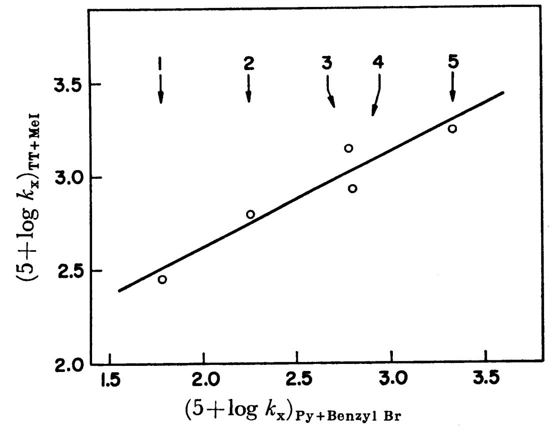


Fig. 3. Empirical correlations for the rate constants. Ordinate; present system, abscissa; pyridine+benzyl bromide, 1: bromobenzene, 2, cyclohexanone, 3; nitrobenzene, 4; methanol, 5; acetonitrile.

An empirical correlation exists[1] among log k_x values in spite of the different nucleophilic centers in the reactants (Fig. 3). The slope of the plots, which gives a relative sensitivity of the reaction to varying solvent characteristics, is smallest for the present reaction. This indicates that the charge development at the transition state is fairly small as compared with the quaternization reaction, or alternatively that charge delocalization in the thiazoline ring reduces the charge density on each atom, thus causing the reaction to be less sensitive to the solvent change.

The observation that the reverse rate process is also liable to solvent effects makes the first suggestion more plausible.

Table 1. Comparison of rate constants, k_f (30 °C)

Solvent	$k_f \times 10^4$	$k_x \times 10^2$
Propylene carbonate	20.5	2.40
Nitrobenzene	14.8	1.43
N,N-Dimethylacetamide	12.3	1.32
Acetonitrile	9.50	1.78
Methanol	3.48	0.849
Cyclohexanone	6.40	0.611
Bromobenzene	2.97	0.280

k_f; l mol^{-1} s^{-1}, k_x; s^{-1}.

Table 2. Comparison of the slopes

Reaction	$\Delta\log k/(\Delta\log k)_{Benzyl\ Br+Pyr}$
Benzyl bromide+Pyridine	1.0[1]
Methyl iodide+Pyridine	0.82[1]
ω-Bromoacetophenone+α-Picoline	0.68[1]
Methyl Iodide+TT	0.51

Pressure Effects and the Volume Change of Reaction. Activation volumes and pressure derivatives were determined by the least squares method after expanding the rate constants into power series of pressure as given by equations 18—20 and are summarized in Table 3.

$$\ln k_p = \ln k_0 + Bp + Cp^2 \tag{18}$$

$$\Delta V_0^{\neq} = (-1)BRT \tag{19}$$

$$(\partial\Delta V^{\neq}/\partial p)_0 = (-2)CRT \tag{20}$$

Table 3. Activation volumes and the pressure derivatives (30 °C)

Reaction	Solvent	$\Delta V_0^{\neq}$ (cm^3 mol^{-1})	$(\partial\Delta V^{\neq}/\partial p)_0$ (cm^5 mol^{-1} kg^{-1})
MeI+Pyr	AN	−25.8	0.0106
MeI+Pyr	PC	−19.7	0.00941
MeI+TT	AN	−24.9	0.00909
MeI+TT	PC	−16.1	0.00395

The apparent molal volumes of the solute, ϕ_v and the overall volume change in the reaction, $\Delta\phi_v$, are summarized in Table 4. In acetonitrile and propylene carbonate, the values of $\Delta\phi_v$ in the table would approximately be equal to the volume change of the reaction, $\Delta\bar{V}°$, since the association constants of the quaternary ammonium salts are usually small in these solvents.[9,10]

We see that the molal volumes of electrolytes are fairly small in acetonitrile as compared to those in propylene carbonate and that there is a near parallelism between the values of $\Delta V_0^{\neq}$ and of $\Delta\phi_v$, resulting in a nearly constant value of $(\Delta V_0^{\neq}/\Delta\phi_v)$.

$\Delta V_0^{\neq}$ is generally considered as the sum of two terms, $\Delta_1 V^{\neq}$, $\Delta_2 V^{\neq}$. The first term arises from changes in the molal volume of the reactant molecules as they form a transition state, while the latter is attributed to the volume change in the surrounding solvents due to electrostriction. A similar dissection of $\Delta\bar{V}°$ in terms of $\Delta_1\bar{V}°$ and $\Delta_2\bar{V}°$ is valuable for the following discussions.

Stewart and Weale[11] concluded that $\Delta_1\bar{V}°\approx 0$, by combining the calculated values of $\Delta_1 V^{\neq}$ for the forward and reverse Menschutkin reactions on the basis of a cylinder model. An alternative estimation of $\Delta_1\bar{V}°$ is possible by the substitution of the molal volume of methylpyridinium iodide by the molar volumes of neutral model compounds, *i.e.*, by the molar volume of toluene as a model compound for methylpyridinium ion, 107.4 cm^3 mol^{-1},[3] and of liquid xenon, 37.3 cm^3 mol^{-1} (−109 °C),[12] (or a little larger than this because of volume expansion due to temperature rise from −109 to 30 °C), as a model compound for iodide, thus leading to $\Delta_1\bar{V}°\approx 107.4+37.3-(81.6+67.1)=-4$ to 0 (cm^3 mol^{-1}). Both estimates suggest that the major part

TABLE 4. APPARENT MOLALVOLUMES AND ACTIVATION VOLUMES (30 °C)

Reaction	Solvents	ϕ_V (cm$_3$ mol^{-1})			$\Delta\phi_V$	$\Delta V_0^{\neq}$	$(\Delta V_0^{\neq}/\Delta\phi_V)$
		Pyr.	MeI	MePyr$^+$I^{-1}			
MeI+Pyr.	AN	81.6	67.1	98.9	−49.8	−25.8	0.52
MeI+Pyr.	PC	81.3	65.1	116.3	−30.1	−19.7	0.65

Reaction	Solvents	ϕ_V (cm^3 mol^{-1})			$\Delta\phi_V$	$\Delta V_0^{\neq}$	$(\Delta V_0^{\neq}/\Delta\phi_V)$
		TT	MeI	MTT$^+$I$^-$			
MeI+TT	AN	145.2	67.1	166.9	−45.4	−24.9	0.55
MeI+TT	PC	151.8	65.1	191.3	−25.6	−16.1	0.63

of the observed values of $\Delta\phi_V$ comes from the term, $\Delta_2\bar{V}^\circ$.

The observed molal volume of a solute V_M is usually larger than the calculated van der Waals volume, V_W, and the ratio (V_M/V_W) is known to range from 1.3 to 2.2 because of the existence of empty space in the liquid.[13] Calculation of van der Waals volumes as proposed by Edward[13] gives the factor (V_M/V_W) of 1.8 and 2.0 for pyridine and methyl iodide in acetonitrile.

Stewart and Weale[11] estimated $\Delta_1 V^{\neq}=-6.5$ cm^3 mol^{-1} for the forward Menschutkin reaction on the basis of the cylinder model. A combination of the value −6.5 and the above factor of 1.8 gives $\Delta_1 V^{\neq}=-11.7$ cm^3 mol^{-1}, which is in reasonable agreement with the estimated value of -10.7 cm^3 mol^{-1} obtained by a completely different method.[14]

The values of $\Delta_2 V^{\neq}/\Delta_2\bar{V}^\circ$ would serve as indices of the degree of charge development at the transition state throughout the series of reactions of the same volume profile along the reaction coordinate, *i.e.*, a slightly modified version of the proposals.[15,16] Making use of the value of $\Delta_1 V^{\neq}=-11.7$ cm^3 mol^{-1} and the above conclusion that $\Delta\phi_V\approx\Delta_2\bar{V}^\circ$, we find that the value $(\Delta_2 V^{\neq}/\Delta_2\bar{V}^\circ)$ becomes nearly constant at 0.26—0.29 for both reactions. An exception is the reaction of TT with methyl iodide in propylene carbonate for which a rather large uncertainty should be included in the value of $\Delta_2 V^{\neq}$ obtained above. Abraham estimated the above indices as 0.4—0.41 from a comparison of the transfer free energy of the activated complex with that of the product ion-pair.[17] Our value of 0.26—0.27 is intermediate between the value 0.2 as estimated previously[1] and the value given by Abraham.[17]

The relative sensitivity difference to change of solvent observed in the case of the reaction rate constants is manifested neither on the activation volumes nor on the values of $(\Delta V_0^{\neq}/\Delta\phi_V)$.

Thus, the desirability of acquiring reliable values of $\Delta_1 V^{\neq}$ and $\Delta_1\bar{V}^\circ$ is obvious.

CNDO/2 Calculation. CNDO/2 calculations[18] were carried out for estimated structures of the transition state using model compounds.[19—21] In order to save time it was assumed that the reaction proceeds through a transition state which has a structure closely resembling a product, *i.e.*, ∠N–C–I=180° for pyridine and methyl chloride, and ∠C(ring)–S–C(methyl)=101° for TT with methyl chloride. Thus only two bond distances r_{N-C} and r_{C-Cl} change during the course of reaction, the others remaining unchanged. The central CH_3 group was assumed to lie in a plane. Calculations were repeated until a minimum total energy was reached, by changing the value of Δr according to $r_{N-C}=1.47+\Delta r$ (or $r_{S-C}=1.80+\Delta r$) and $r_{C-Cl}=1.78+\Delta r$, where the numerals indicate normal bond distances of a model compound.[19—21]

Charge densities for the minimized structures as given in Figs. 4 and 5 suggest that electronic charges are more developed at the transition state for the reaction of pyridine with methyl iodide, which corresponds to the arguments put forward on the basis of the rate studies.

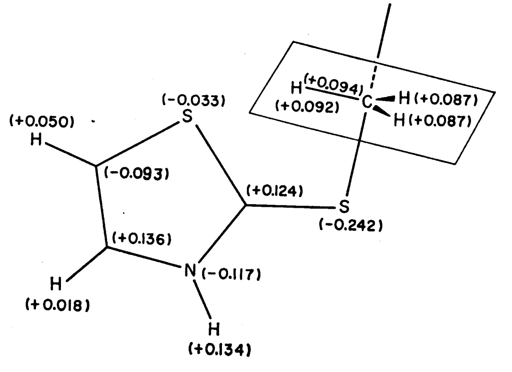


Fig. 4. Charge distribution for minized structure. $r_{C-S}=1.83$ Å, $r_{C-Cl}=1.81$ Å, $\mu=6.74$ D.

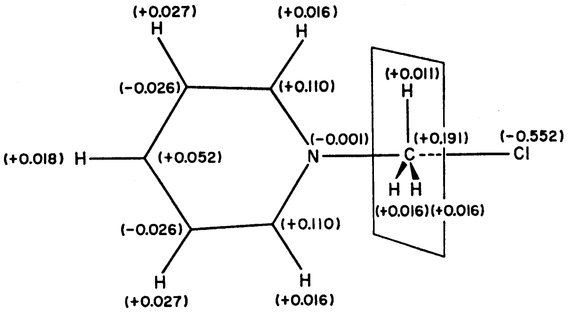


Fig. 5. Charge distribution for minimized structure. $r_{N-C}=1.59$ Å, $r_{C-Cl}=1.90$ Å, $\mu=10.7$ D.

Heydtman *et al.*[22] estimated the dipole moment of the activated complex to be 7.8 D by applying the Kirkwood approach[23] to the reaction of ω-bromoacetophenone with α-picoline. Eckert *et al.* derived a value of 5.9 D for the reaction of pyridine and methyl iodide by the same approach.[24] For the reaction of pyridine with methyl iodide, the slope of the plots of $RT \ln k$ *vs.* $(D-1/2D+1)$ corresponds to 14.3 kcal mol^{-1}. This leads to the value 6.3 D for the dipole moment of the activated complex, when allowance is made for the empty space as mentioned above, *i.e.*, the factor of 1.8, and when radii are calculated from the molal volumes in Table 4 assuming a spherical molecule. A different application of the Kirkwood approach leads to a different dipole moment as described by Eckert.[25] Thus, the model CNDO/2 calculation provides an alternative way of estimating the dipole moment.

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