Nonequilibrium Solvent Polarization in Kinetics of S_N2 Reactions

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ABSTRACT: The solvent effect on the experimental activation barriers for the reactions of methyl iodide with chloride and thiocyanate ions was analyzed according to the Marcus and Shaik theories, considering $S_N 2$ mechanism in terms of a single electron shift. The linear increase in the solvent reorganization energy of the Marcus theory (after removing contributions from the specific solvation) with the solvent Pekar factor, describing the effect of the nonequilibrium solvent polarization, was observed for six aprotic solvents. The direct support of the title effect based on the Shaik theory was less evident; however, in general, the calculated activation barriers in 10 solvents change parallel with the experimental ones. © 2002 Wiley Periodicals, Inc. Int J Chem Kinet 35: 61–66, 2003

INTRODUCTION

The description of the $S_N 2$ mechanism as a single electron shift synchronized in a one-step reaction to the bond interchange and solvent reorganization has been repeatedly examined since the original proposition of Shaik and Pross [1–7] based on the curve crossing or state correlation diagrams. The unified theory for the rates of the $S_N 2$ and electron transfer (ET) reactions was also proposed by Marcus [8]. Both models were successful in comparison with the experimental results obtained in the gas phase and aqueous solutions [3,6–8]; the first model was successful even in comparison with the results obtained in DMF [3,6,7]. Considering solvent effects on the $S_N 2$ rate constants, both models take into account an important contribution to the activation free energies originated from the nonequilibrium

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solvent polarization in the transition state (TS). This contribution results from a slow reorientation of solvent molecules that cannot follow the instantaneous position of the electronic charge in the TS and therefore they adjust to some averaged charge distribution [8]. In the Marcus theory [8] this contribution is described by the solvent reorganization energy λ_0 , which depends (according to a simplified dielectric continuum model) on the solvent Pekar factor $\gamma_{solv} = \frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}$ related to the static ε_s and optical ε_{op} electric permittivity ($\varepsilon_{\rm op} \approx n_{\rm D}^2$). Contributions of λ_0 to the activation barriers are well documented experimentally (by the dependences of intrinsic activation barriers on the Pekar factor) in the case of outer-sphere ET processes and the bond cleavage of radical anions [9,10], which can be described [11] as a concerted bond-breaking and an intramolecular electron shift. On the other hand, the effect of the nonequilibrium solvent polarization in the TS for S_N2 reactions was not directly demonstrated using experimental results in a number of solvents [1–8] until our recent work [12]. It was shown [12] on the basis of the Marcus theory [8] that the intrinsic activation free energy for the reaction between methyl iodide

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and chloride ions in six aprotic solvents, after removing the contribution of the specific solvation, increases linearly with the solvent Pekar factor. A similar analysis for the reaction of methyl iodide with thiocyanate anions for which the rate constants were measured in 10 solvents (the greatest number in the Parker compilation [13]) as well as a comparison with predictions of the Shaik theory [6,7] for both reactions are presented here.

RESULTS AND DISCUSSION

Solvent Analysis in Terms of the Marcus Theory [8]

A similar approach based on the Marcus theory [8] as used previously [12] for reaction (1):

$$Cl^- + MeI \rightarrow MeCl + I^-$$
 (1)

was applied to reaction (2):

$$SCN^{-} + MeI \rightarrow MeSCN + I^{-}$$
 (2)

The values of the activation barrier $\Delta G^{\ddagger}_{exp}$ were calculated from the experimental rate constants extracted from the Parker compilation [13] assuming [12] the preexponential term to be equal to $10^{12} \text{ M}^{-1} \text{ s}^{-1}$. The values obtained are shown in Table I and it is evident that they are strongly solvent-dependent, changing from 67 kJ mol⁻¹ in *N*-methylpyrrolidinone (NMP) to 89 kJ mol⁻¹ in water.

Table IActivation Free Energy and Its ComponentsAccording to Marcus Theory for the Reaction (2) of Melwith SCN⁻ in Different Solvents

Solvent	$\Delta G^{\ddagger}_{exp}$ (kJ mol ⁻¹)	$-0.5\Delta G^{\circ}$ (kJ mol ⁻¹)	$w_{\rm r} + \lambda_0/4$ (kJ mol ⁻¹)	$\frac{\lambda_0/4 + C}{(kJ \text{ mol}^{-1})}$
H ₂ O	88.5	6.5	65	37
MeOH	87.3	5.5	63	42
FA ^a	84.5	6.3	61	39
NMF^b	82.2	6.0	58	38
MeNO ₂	79.9	5.5	55.5	42
ACN^{c}	79.3	5.3	55	42
DMF	74.8	5.0	50	38
AC^d	73.1	6.0	49	39
DMA	73.1	6.5	50	38
NMP ^e	67.4	6.0	44	34

^a Formamide.

^bN-Methylformamide.

^cAcetonitrile.

^d Acetone.

^e N-Methylpyrrolidinone.

The thermodynamic driving force was calculated [8,12] as

$$\Delta G^{\circ\prime} = F \Delta E^{\circ} + D_{\text{MeI}} - D_{\text{MeSCN}} \tag{3}$$

where ΔE° is the difference between formal potentials for I/I⁻ and SCN/SCN⁻ redox couples, and D_{MeI} and D_{MeSCN} are the energies of homolytic bond dissociation in the compound indicated. Formal potentials in different solvents were calculated from those in aqueous solutions ($E^{\circ} = 1.4$ V vs. NHE for I/I⁻ and $E^{\circ} = 1.66$ V vs. NHE for SCN/SCN⁻ [14,15]) and the free energy of transfer of each anion from water to a given solvent [16]; only for acetone (Ac) and Nmethylformamide (NMF), where free energies of transfer are unknown, the proper values were estimated using the dependence on the Dimroth and Reichardt E_{T}^{N} solvent parameter [17]. Taking into account the fact that solvent effects on D_{MeI} and D_{MeCl} are very small [12] the solvent-independent value of $D_{\text{MeI}} - D_{\text{MeSCN}} =$ -38 kJ mol⁻¹ was used in Eq. (3). The last value was estimated for the aqueous solution using $\Delta G^{\circ\prime} =$ -13 kJ mol^{-1} as suggested by Pearson [15] on the basis of the gas-phase dissociation energy $D_{\text{MeSCN}} =$ 293 kJ mol^{-1} .

The values of $\Delta G^{\circ'}$ obtained in a number of solvents are shown in Table I. The solvent change of $\Delta G^{\circ'}$ is only 3 kJ mol⁻¹, which is very small as compared with an analogous change (Table II) for reaction (1) [12]. The main reason of this small solvent change is a similar solvent effect on ΔG°_{tr} of I⁻ and SCN⁻ ions, whereas this effect is much higher for Cl⁻ ions. As a result, free

Table II Activation Free Energy in Different Solvents for Reactions $Y^- + MeI \rightarrow MeY + I^-$ Calculated According to the Shaik Theory

		$Y^- = Cl^-$		$Y^- = SCN^-$	
Solvent ^a	$ ho^b$	$-\Delta G^{\circ}$ (kJ mol ⁻¹)	$\Delta G^{\ddagger}_{calc}$ (kJ mol ⁻¹)	$\Delta G^{\ddagger}_{calc}$ (kJ mol ⁻¹)	
H ₂ O	0.56	-3	124	119	
MeOH	0.55	0	120	117	
FA	0.47	3	106	103	
NMF	0.49	_	_	106	
MeNO ₂	0.51	13	105	108	
ACN	0.54	21.5	104	113	
DMF	0.48	22	94	103	
AC	0.52	20	99	108	
DMA	0.47	27	90	100	
NMP	0.53	28	98	110	

^a For solvent abbreviations see footnote to Table I.

^bSolvent reorganization factor from Ref. [7] or calculated from data in Ref. [21].

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energies of activation for reaction (2) do not depend on the thermodynamic driving force $\Delta G^{\circ'}$.

Assuming the same approximation for the resonance energy of interactions of the states as used previously [12], the activation free energy according to the Marcus model [8] can be described by Eq. (4):

$$\Delta G^{\ddagger} = w_{\rm r} + 0.25\lambda_0 + 0.06(D_{\rm MeI} + D_{\rm MeSCN}) + 0.5\Delta G^{\circ\prime}$$
(4)

Assuming further that the solvent effect on $0.06(D_{\text{MeI}} + D_{\text{MeSCN}})$ is negligibly small, as was found for the reaction with Cl⁻ ions [12], the component $w_{\text{r}} + 0.25\lambda_0$ (Table I) was calculated for a constant value of $0.06(D_{\text{MeI}} + D_{\text{MeSCN}}) = 29.9$ kJ mol⁻¹; the last value was estimated for the aqueous solution.

It is evident that the sum of the work term and the solvent reorganization energy $w_r + 0.25\lambda_0$ gives the main contribution to the solvent effect on the activation free energy. There is no clear dependence of the sum $w_r + 0.25\lambda_0$ on the solvent Pekar factor γ_{solv} ; however, separate correlations for the groups of protic and aprotic solvents can be observed, as shown in Fig. 1.

On the other hand, the acceptable correlation was found with the E_T^N solvent parameter:

$$w_{\rm r} + 0.25\lambda_0 = 28(\pm 9)E_{\rm T}^{\rm N} + 39(\pm 5)$$

$$n = 10, r = 0.937, F = 51.1, \delta = 2.3$$
(5)

where *n* is the number of solvents, *r* the correlation coefficient, *F* the value of the Snedecor test, and δ



Figure 1 Dependence of the sum of the work term and the solvent reorganization energy for the reaction of MeI with SCN^- on the solvent Pekar factor. Solvent abbreviations as in Table I.

the mean quadratic deviation from the correlation line; 95% errors of regression coefficients are given in parentheses. A similar dependence was found previously [12] for the reaction with Cl⁻ ions and was discussed as the manifestation of specific solvation effects on the work term (which involves a partial desolvation of anions) and/or on the solvent reorganization energy (the noncontinuum effect not included in the Pekar factor [12]). In order to remove this specific solvent effect, the term 28 $E_{\rm T}^{\rm N}$, i.e., the slope from Eq. (5), was subtracted from the sum $w_r + 0.25\lambda_0$ giving $0.25\lambda_0 + C$, where C is a solvent-independent constant. The values of $0.25\lambda_0 + C$ are shown in Table I. They depend on the Pekar factor for six aprotic solvents (Fig. 2) giving the following correlation with the intercept equal to zero:

$$0.25\lambda_0 + C = 81(\pm 3)\gamma_{\text{solv}}$$

 $n = 6, r = 0.920, F = 27.4, \delta = 1.05$
(6)

A similar correlation found [12] for reaction (1) is also shown in Fig. 2. If the null intercept in Eq. (6) indicates that the specific solvation of negative charge in the TS and connected with the work term were completely removed, then the constant C = 0 and the obtained values are equal to $0.25\lambda_0$ and can be described by the classic Marcus expression [8]:

$$0.25\lambda_0 = (e^2/4)(1/2a_1 + 1/2a_2 - 1/R) \\ \times (1/\varepsilon_{\rm op} - 1/\varepsilon_{\rm s})$$
(7)



Figure 2 Relationships between the solvent reorganization energy (without the contribution from the specific solvation) and the solvent Pekar factor for reactions of MeI with SCN⁻ (circles) and Cl⁻ (squares, data from Ref. [12]). The correlation lines for aprotic solvents (solid points) are shown. Solvents: 1 - NMP, 2 - DMF, 3 - DMA, 4 - AC, $5 - MeNO_2$, 6 - ACN.

where a_1 and a_2 represent the radii of spheres of an electron localization and R is the distance between them in the TS, and the term in the last parentheses is the Pekar factor. The comparison of Eqs. (6) and (7) indicates that the same slope (equal to 82) as the experimental one (equal to 81) can be obtained assuming $a_1 = 350$ pm as for the solvated iodide ion [12] but $a_2 = 213$ pm as for bare thiocyanate ion [18] and $R = a_1 + a_2 + 2r = 717$ pm (with r = 77 pm corresponding to the covalent radius of the carbon atom). Thus, the contribution to the intrinsic activation barrier from the nonequilibrium solvent polarization of the TS looks reasonable. Moreover, it can be found that the solvent reorganization energy $0.25\lambda_0$ describing the effect of the nonequilibrium solvent polarization is high for aprotic solvents and represents 46% (in NMP) to 50% (in DMF) of the intrinsic activation barrier. The last effect is a little lower for protic solvents (with the lowest value equal to 39% in water).

It is evident from Fig. 2 that the point for water deviates completely from the correlation line given by Eq. (6) in a similar manner as was previously observed for reaction (1) between MeI and Cl⁻ ions [12]. However, for other protic solvents the points are more close to the correlation line, giving, for n = 9, r = 0.890 but with a high scatter of points ($\delta = 1.13$). Taking into account precision of the estimated data, this means that in general for all solvents, with the exception of water, the nonequilibrium polarization effect in the TS seems to play an important role and the Marcus model [8] can reasonably describe it.

Solvent Analysis in Terms of the Shaik Theory [3,6,7]

The activation barrier for the nonidentity S_N2 reaction was modeled [1-7] in terms of the deformations required to allow resonance between ground and charge transfer states of reactants, i.e., as a result of the avoided crossing between those states. Thus, the activation barrier depends on at least five parameters: two vertical ET energy gaps $G_R = I_{Y:} - A_{RX}$ and $G_P = I_{X:} - A_{RY}$ (where I and A are the vertical ionization potential and the electron affinity, respectively, of indicated species and Y: and X: denote the nucleophile and the leaving group, respectively), two slope factors approximated by the total delocalization indices of the charge transfer states $f_{\rm R} \approx w_{\rm R} (Y^{\bullet}/({\rm R} \rightarrow {\rm X})^{-})$ and $f_{\rm P} \approx w_{\rm R} (X^{\bullet}/({\rm R} \rightarrow {\rm X})^{-})$ $Y)^{-}$), and the avoided crossing interaction B (i.e., a measure of the resonance energy in the TS) taken usually [3,6,7] as a constant equal to ca. 58.6 kJ mol⁻¹. In the free energy notation the full activation barrier is approximated [6,7] by

$$\Delta G^{\ddagger} \approx [f_{\rm R} + f_{\rm P} + (1 - f_{\rm R} - f_{\rm P})\Delta G^{\circ}/G_{\rm R}] \\ \times G_{\rm R}G_{\rm P}/(G_{\rm R} + G_{\rm P} - \Delta G^{\circ}) - {\rm B}$$
(8)

Energy gaps for the vertical electron transfers in solution can be approximated [3,7] using the gas-phase energy gaps and solvation free energies of both anions $S_{Y:}$ and $S_{X:}$ and radical anion $S_{(R-\cdot)^-}$

$$(I_{Y:} - A_{RX})_{s} \approx (I_{Y:} - A_{RX})_{g} + (1 + \rho)S_{Y:}$$
$$- (1 - \rho)S_{(R-\cdot)^{-}} \approx (I_{Y:} - A_{RX})_{g}$$
$$+ S_{Y:} - S_{X:} + \rho(S_{Y:} + S_{X:}) \qquad (9)$$

$$(I_{X:} - A_{RY})_{s} \approx (I_{X:} - A_{RY})_{g} + S_{X:} - S_{Y:}$$

 $+\rho(S_{Y:} + S_{X:})$ (10)

where the solvent reorganization factor $\rho = (\varepsilon_s - n_D^2)/[n_D^2(\varepsilon_s - 1)]$ [3,6,7] is a function of the static electric permittivity and the refractive index.

It is more convenient to analyze the solvent effect on the total energy barrier according to the above equations than to separate the intrinsic barrier as in the Marcus model. For the reaction between chloride ions and MeI (reaction (1)) the gas-phase energy gaps [7] are equal to $(I_{\text{Cl}:} - A_{\text{MeI}})_{\text{g}} = 389.1 \text{ kJ mol}^{-1}$ and $(I_{\text{I}:} - A_{\text{MeCI}})_{\text{g}} = 422.6 \text{ kJ mol}^{-1}$, the slope factors in all aprotic solvents were assumed to be the same as in DMF [7] ($f_{\text{R}} = 0.243$, $f_{\text{P}} = 0.242$) and in all protic solvents to be the same as in water ($f_{\text{R}} = 0.239$, $f_{\text{P}} = 0.243$). The solvation free energies were calculated using the free energy of transfer of a given anion from water to a given solvent [16] and absolute standard molar Gibbs free energies of hydration equal to $S_{\text{Cl}:} = 347 \text{ kJ mol}^{-1}$ and $S_{\text{L}:} = 283 \text{ kJ mol}^{-1}$ [19].

The reaction with thiocyanate ions (reaction (2)) was not considered previously [3,6,7]. The gas-phase ionization potential of the nucleophile $I_{\text{SCN:(g)}} = 224 \text{ kJ}$ mol⁻¹ was estimated from the correlation (r = 0.995) of $I_{Y:(g)}$ for five nucleophiles (H₂N', H₂P', HO', HS', and CN' taken from Table 4.1 in Ref. [7]) with the electron affinity of corresponding radicals [20], and the vertical gas-phase electron affinity of MeSCN was calculated from the bond dissociation energies of the molecule and the radical anion using the following equation [3,7]:

$$A_{\rm RY} = A_{\rm Y.} - D_{\rm R-Y} + D_{\rm R-Y}$$
 (11)

where $A_{Y} = 224 \text{ kJ mol}^{-1}$, $D_{R-Y} = 293 \text{ kJ mol}^{-1}$ (as estimated in the previous part), and $D_{R-Y} = -86 \text{ kJ mol}^{-1}$; the last value was estimated from the correlation

(all values in kcal mol^{-1}):

$$D_{\text{R-}\cdot\text{Y}} = -0.31(\pm 0.03)A_{\text{Y}} - 3.9(\pm 1.9)$$

$$n = 9, \ r = 0.993, \ F = 532, \ \delta = 0.74$$
(12)

found for nine leaving groups (F, Cl, Br, I, HO, MeO, HS, MeS, H₂N) using data from Table 4.3 in Ref. [7]; finally, $A_{MeSCN(g)} = -155$ kJ mol⁻¹. The value of $f_P = 0.311$ in water (and other protic solvents) was estimated from the suggested [6] dependence on $1/(A_{\rm Y}. - A_{\rm R}.)^2$ with $A_{\rm R}.$ = constant, using f_P values [6,7] for PhS, HS, HO, and CN and their oxidation potentials in water [15] as the approximation of solution $A_{\rm Y}$. values. A slightly higher value of $f_P = 0.313$ was assumed for aprotic solvents [6,7]. The free energy of hydration of SCN⁻ ion is $S_{\rm SCN:} = 287$ kJ mol⁻¹ [19] and in other solvents the corresponding values were obtained from the free energy of transfer of that anion [16].

Activation free energies for reactions (1) and (2) calculated according to Eqs. (8)–(10) are given in Table II. The free energy ΔG° of reaction (1), based on the literature data [12,22], is also given therein; it can be added that ΔG° does not include free energy of the formation of ion-dipole complexes of reactants and products, which is contrary to $\Delta G^{\circ'}$ from Marcus theory, but in Eq. (3) the work terms were also neglected. For the reaction with chloride ions (reaction (1)) the comparison of the calculated and experimental activation barriers, shown in Fig. 3, indicates a rather weak dependence; excluding the most deviating point for formamide (FA) it gives the following correlation line



Figure 3 The relationship between the experimental activation barrier for reactions of MeI with SCN⁻ (open squares) and Cl⁻ (solid circles) ions and the barrier calculated according to the Shaik theory. The correlation line described by Eq. (13) for the second reaction (without FA) is shown.

(as shown in Fig. 3):

$$\Delta G^{\ddagger}_{calc} = 0.7(\pm 0.2) \Delta G^{\ddagger}_{exp} + 49(\pm 12)$$

$$n = 8, r = 0.959, F = 68.6, \delta = 3.2$$
(13)

For reaction (2), the observed scatter of points is substantially greater with the same most deviating points for FA and NMP, but a similar general trend is observed.

It should be stressed here that the $\Delta G^{\ddagger}_{calc}$ values were calculated against the free energy of ion-dipole complexes of reactants but experimental barriers include the formation of these complexes. The last effect was discussed [7] in terms of a part of solvation free energy of an anion S_{Y_i} but the addition of S_{Y_i} as the second explanatory parameter to Eq. (13) is statistically not significant. Moreover, it is evident from Fig. 3 that the calculated values for both reactions are much higher than the experimental ones. The same tendency was found [7] but not explained for a number of $S_N 2$ reactions in aqueous solutions where the calculated activation barriers were 16-32% higher than experimental ones and in DMF where they were 32-40% higher. In contrast to that, the calculated and the experimental values in the gas phase were similar [7]. The possible explanation of higher activation barriers in solutions, as suggested by a referee, can be caused by neglecting the intermolecular term in the simplified calculation of the reorganization factor ρ , which was originally estimated [3,7] on the basis of the solvation of individual ions (e.g. nucleophile) instead of a molecular complex (i.e. the transition state).

In conclusion, the plots shown in Fig. 3 indicate that solvent effects on the activation barriers for reactions of interest calculated using the Shaik theory in general reflect the observed trends but the direct support of a fundamental role of the nonequilibrium solvent polarization in TS is difficult to obtain. On the other hand, using the Marcus theory the direct support is evident at least for aprotic solvents; however, in aqueous solutions some additional effects should be taken into account.

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