

COMMUNICATIONS

LETTERS

Cooperative Effect of Solvent Polarity and Hydrogen Bond Donor Acidity on S_N1 Solvolyses Rates in MeOH-MeCN MixturesIkchoon Lee[†], Bon-Su Lee, In sun Koo and Se Chul Sohn

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Various anomalies in physico-chemical properties of MeOH-MeCN mixtures have been reported at the composition of 80~90% (v/v) MeOH¹, which are often attributed to the broken down polymer chain structure of MeOH. In a recent paper² we reported maximum behaviors in selectivity parameters, Hammett ρ_N , ρ_S and Brønsted β values, at this solvent composition for the reactions of substituted benzenesulfonyl chlorides (ρ_S) with anilines (ρ_N). We ascribed the phenomena to the maximum ionizing power of the solvent mixture.

We wish here to report similar maximum behaviors but the maximum occurring at a different solvent composition of MeOH-MeCN mixtures depending on the leaving group in the S_N1 solvolysis of *t*-butyl halides.

Rate constants for the solvolysis of *t*-butyl chloride, -bromide and -iodide in MeOH-MeCN mixtures were determined conductometrically² and the results are summarized in Table 1. We note that there are rate maxima at solvent compositions of 80~90%, 70~80% and 50~60% MeOH for *t*-butyl chloride, bromide and iodide respectively.

Taft's solvatochromic parameters³ π^* , a polarity scale, and α , a hydrogen bond donor (HBD) acidity scale, were then determined by averaging three values each obtained from substitutions of k values in Table 1 into the three solvatochromic equations, of the type $\log k = \text{const} + s\pi^* + a\alpha$, for the three halides reported by Taft et al.,^{3,4}

$$\begin{aligned} \log k (t\text{-BuCl}) &= -15.06 + 6.94 \pi^* + 5.25 \alpha \\ \log k (t\text{-BuBr}) &= -12.41 + 7.21 \pi^* + 3.95 \alpha \quad (1) \\ \log k (t\text{-BuI}) &= -10.52 + 6.86 \pi^* + 2.71 \alpha \end{aligned}$$

The two scales thus obtained are given in Table 2 and are presented graphically in Figure 1. We note that the trends of changes in π^* and α with the variation of solvent composition are opposite; π^* decreases while α increases with the increase in MeOH content. Addition of two curves, $\pi^* + \alpha$,

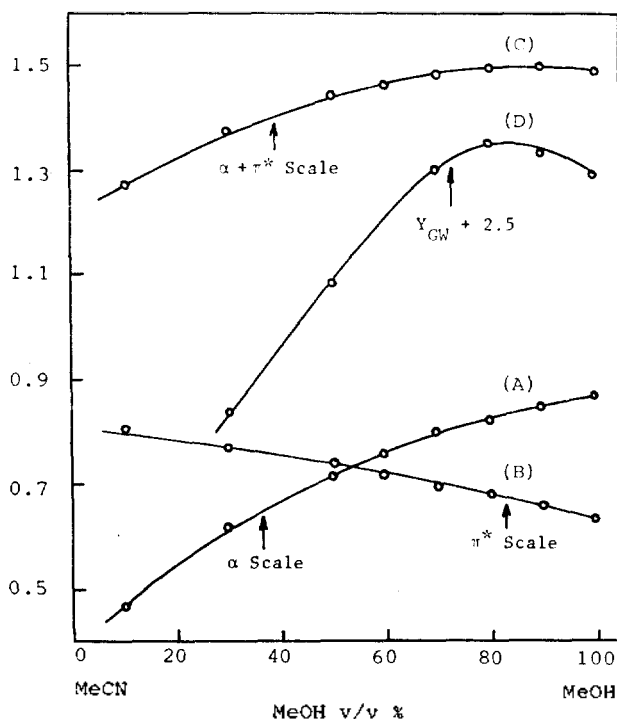


Figure 1. Plots of α , π^* , $\alpha + \pi^*$ and Y_{GW} values vs. volume % of MeOH in MeOH-MeCN mixtures.

which should be a measure of solvent ionizing power, is seen to exhibit a maximum at ~90% MeOH. Comparison of this curve, $\pi^* + \alpha$, with that of the Winstein Y obtained from Table 1 does not show exact correspondence. This is apparent from the a/s values for the two cases; the former has a value of $a/s = 1.0$ whereas the latter has a value of 0.75.

Plots of the function $s\pi^* + a\alpha$ with $a/s \approx 0.75, 0.55$ and 0.40 (which are values obtained from eq. (1) for the three *t*-butyl halides) actually gave maxima at solvent compositions of 80~90%, 70~80% and 50~60% MeOH corresponding to our maxima positions in $\log k_{25^\circ}$ versus composition plots

TABLE 1: Rate Constants^a for the Solvolysis of *t*-Butyl Halides in MeOH-MeCN Mixtures

Compounds	MeOH (v/v %)	Temperatures			
		25.0 °C	35.0 °C	45.0 °C	55.0 °C
<i>t</i> -BuCl $k_1 \times 10^6$ (sec ⁻¹)	100	0.752 ^b	3.48±0.03	12.0±0.4	38.2±0.2
	90	0.822	3.62±0.03	14.0±0.2	44.2±0.3
	80	0.869	3.60±0.02	14.4±0.3	40.9±0.5
	70	0.779	3.30±0.04	13.3±0.2	38.3±0.3
	50	0.594	2.33±0.05	9.63±0.04	24.5±0.4
	30	0.285	—	5.51±0.01	15.3±0.3
<i>t</i> -BuBr $k_1 \times 10^5$ (sec ⁻¹)	100	3.65±0.05	12.9±0.1	46.7±0.3	
	90	4.39±0.01	14.5±0.1	51.7±0.1	
	80	4.75±0.05	15.5±0.1	53.4±0.1	
	70	4.92±0.03	15.1±0.1	51.5±0.4	
	60	4.63±0.02	—	—	
	50	4.22±0.03	12.6±0.2	41.6±0.3	
<i>t</i> -BuI $k_1 \times 10^4$ (sec ⁻¹)	100	1.43±0.40	4.64±0.10	15.5±0.1	
	90	1.80±0.03	6.34±0.01	18.1±0.4	
	80	2.10±0.03	7.13±0.05	23.0±0.2	
	70	2.26±0.02	8.12±0.10	25.0±0.2	
	60	2.41±0.04	8.73±0.09	26.0±0.1	
	50	2.51±0.03	8.79±0.05	25.6±0.2	
	30	2.37±0.02	7.45±0.01	21.0±0.1	
	10	1.79±0.01	5.38±0.01	16.6±0.2	

^a Mean of two or three kinetic runs. Errors shown are standard deviations.

^b k_1 values for *t*-BuCl at 25 °C are extrapolated values from Arrhenius plots.

TABLE 2: Solvatochromic Parameters π^* and α Values

MeOH (v/v %)	100	90	80	70	60	50	30	10
α	0.868	0.846	0.820	0.796	0.752	0.712	0.614	0.469
π^*	0.630	0.654	0.676	0.688	0.712	0.734	0.762	0.802

for *t*-butyl chloride, -bromide and -iodide respectively.

Two important conclusions can be drawn: (i) a maximum behavior in the S_N1 rate constants is a result of cooperative effect of solvent polarity, π^* , and HBD acidity, α , of solvent mixtures. In this sense, the ionizing power of solvent⁵ we speak of loosely is composed of two effects, π^* and α , and should be given as curve C in Figure 1. (ii) as expected, HBD acidity, α , is more important for chloride whereas polarity, π^* , is more important for the more polarizable iodide and the two have comparable effects for bromide.

Reference to eq. (1) reveals that "s" values are nearly the same, (~7.0) for the three substrates but "a" values differ significantly (2.7–5.5) since HBD acidity affects only the leaving group anions. This implies that at the transition state (TS) charge development for the three substrates is nearly the same since the stabilization of TS by the solvent polarity i. e., susceptibility of rates to π^* scale change is nearly the same. However in order to have such degree of charge development at the TS, assistance of stronger HBD acidity is needed for the chloride compared to the other two halides. We would therefore expect that in the solvolysis of substituted benzenesulfonyl chlorides, will have an equal "a" but different "s" values as substituent is varied, since here the degree of

charge development will be different at the TS depending on the substituent of the substrate. We have confirmed this effect with several series of compounds and full results will be reported elsewhere.

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The Critical Dynamics for the Two-Dimensional Two-Spin Exchange Ising Model

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Kawasaki¹ has studied the diffusion constant of spins in ferromagnets or molecules in binary mixtures near the critical point with the aid of the terminology of the spin system. His model is a time-dependent Ising model in which spin interactions are replaced by certain temperature-dependent transition probabilities of spin exchange. The transition probability of spin exchange is so chosen as to give the same equilibrium spin distribution function as conventional Ising system. In this respect, his model is quite similar to Glauber's, but is different from his in that the total spins are conserved at each transition. Achiam and Kosterlitz² have proposed a real-space renormalization group (RG) technique to treat dynamic critical phenomena in two-dimensional Ising model, which is just the extension of the real-space static RG method developed by Niemeijer and van Leeuwen³ and Kadanoff and Houghton⁴. Their model is that proposed by Glauber in which only one spin flips independently at a time from one state to another according to the prescribed transition probability. In this letter, we extend the RG method in real-space to Kawasaki's Ising model with two spin exchange. Then, we obtain a dynamic exponent for energy fluctuations.

The system we shall consider is a homogeneous two-dimensional Ising system. Let us apply a weak external force to the system at equilibrium. Then, the system will relax towards the equilibrium through an interaction with a heat reservoir. It is assumed that only two spins exchange at a time during the relaxation. The probability $P(\sigma_j, \sigma_k, \{\sigma\}_{jk}, t)$ for the spin-exchange on which the pair of spins σ_j and σ_k on the sites j and k exchanges each other may be described as

$$\begin{aligned} \tau \frac{\partial}{\partial t} P(\sigma_j, \sigma_k, \{\sigma\}_{jk}, t) \\ = - \sum_{\{jk\}} (1 - p_{jk}) W_{jk}(\sigma_j, \sigma_k, \{\sigma\}_{jk}) P(\sigma_j, \sigma_k, \{\sigma\}_{jk}, t) \\ = - L(\sigma) P(\sigma_j, \sigma_k, \{\sigma\}_{jk}, t), \end{aligned} \quad (1)$$

where τ is the bare relaxation time, p_{jk} the operator to exchange σ_j and σ_k , $W_{jk}(\sigma_j, \sigma_k, \{\sigma\}_{jk})$ the transition probability in which the pair of σ_j and σ_k exchanges each other and $\{\sigma\}_{jk}$ denotes the set of spins except σ_j and σ_k .

It should be noted that the time-displacement operator, L , is Hermitian. As $t \rightarrow \infty$, $P_{eq}(\sigma_j, \sigma_k, \{\sigma\}_{jk})$ satisfies the condition of detailed balance

$$\begin{aligned} W_{jk}(\sigma_j, \sigma_k, \{\sigma\}_{jk}) P_{eq}(\sigma_j, \sigma_k, \{\sigma\}_{jk}) \\ = W_{jk}(\sigma_k, \sigma_j, \{\sigma\}_{jk}) P_{eq}(\sigma_k, \sigma_j, \{\sigma\}_{jk}) \end{aligned} \quad (2)$$

One may choose any specific form of the transition probability which obeys the above condition. We take the similar form of the transition probability used by Achiam and Kosterlitz instead of Kawasaki

$$\begin{aligned} W_{jk}(\sigma_j, \sigma_k, \{\sigma\}_{jk}) \\ = \{P_{eq}(\sigma_k, \sigma_j, \{\sigma\}_{jk}) / P_{eq}(\sigma_j, \sigma_k, \{\sigma\}_{jk})\}^{1/2} \cdot \exp(H_{jk}) \end{aligned} \quad (3)$$

where H_{jk} is the Hamiltonian due to the products of σ_j and σ_k .

It can be seen that $W_{jk}(\sigma_j, \sigma_k, \{\sigma\}_{jk}) P_{eq}(\sigma_j, \sigma_k, \{\sigma\}_{jk})$ is independent of the spins σ_j and σ_k . The equilibrium probability distribution can be described as

$$\begin{aligned} P_{eq}(\sigma_j, \sigma_k, \{\sigma\}_{jk}) = \exp\{-H(\sigma)\} / Z; \\ H(\sigma) = K_2 \sum_{\langle n,n.\rangle} \sigma_n \sigma_n + K_3 \sum_{\langle n,n,n.\rangle} \sigma_n \sigma_n + \dots \end{aligned} \quad (4)$$

where $\langle n,n.\rangle$ and $\langle n,n,n.\rangle$ mean the nearest neighborhood and the next nearest neighborhood, respectively, and the coupling constants K_2 and K_3 are related with the true coupling constants J_2 and J_3 by $K_2 = J_2 / k_B T$ and $K_3 = J_3 / k_B T$. The probability distribution at time t can be parameterized by a time-dependent Hamiltonian through the coupling constants and the partition function at t can be replaced by the equilibrium partition function within the linear response. Applying the RG transformation matrix, $T(\mu, \sigma)$, used in the static case by Niemeijer and van Leeuwen³ and Kadanoff and Houghton⁴ to the probability distribution at t , we obtain the new distribution for the new set of spin variable $\mu (= \pm 1)$ on a lattice with a lattice constant larger by a scaling factor of l

$$\begin{aligned} P'(\mu, t) = \exp\{-H'(\mu, t)\} / Z \\ = \sum_{\{\sigma=\pm 1\}} T(\mu, \sigma) P(\sigma, t); \\ H'(\mu, t) = K_2'(t) \sum_{\langle n,n.\rangle} \mu_n \mu_n + K_3'(t) \sum_{\langle n,n,n.\rangle} \mu_n \mu_n + \dots, \end{aligned} \quad (5)$$