was dried over $MgSO_4$ and distillation under reduced pressure (135°C/4mmHg) afforded the (E)–alkene (**2**) and (Z)–alkene (**1**) (0.08g, 40% yield). The ratio of *trans* (E–) and *cis* (Z–) was 50:50 by gas chromatography with Carbowax 20M on Varian 3700. IR: 3020, 2900, 1740, 1600, 1450, 1360, 1240, 1040, 960, 925, 905, 700 cm^{-1}, NMR:δ5.4 (2H, t, J—8Hz), 4 (3H, t), 2 (4H, s), 1.8–1.1 (21H, m), MS: m/e 194 (M^+–CH_3CO_2H).

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Solvation in Mixed Solvents (IV). Solvolysis of Adamantyl Derivatives in Methanol-Acetonitrile Mixtures

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(*Received October 10, 1984*)

Solvolysis of 1–adamantyl chloride, –bromide and –tosylate have been studied in methanol–acetonitrile mixtures. Rate maxima were found for 1–adamantyl bromide and tosylate at 80–90 % methanol mixtures. The rate maximum observed was interpreted as a result of cooperative enhancement of cation and anion solvation. 1–Adamantyl tosylate had small cation solvation but had extensive anion solvation. It was concluded that the *Y* scale based on adamantyl tosylate is superior to others since it varies in a wide range especially for weakly ionizing medium.

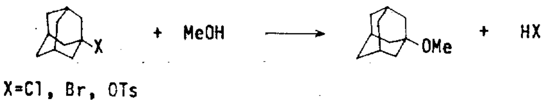
Solvolysis of *tert*–butyl halides have received considerable attention in the study of solvent effects on rates of chemical reactions.[1–7] Grunwald and Winstein[1–3] introduced equation (1) for correlating solvent dependence of rates of organic ractions.

$$\log k = \log k_0 + mY \qquad (1)$$

where k and k_0 are the rates of a reaction in a solvent of ionizing power Y and in the reference solvent, 80% ethanol–water mixture, respectively. The m represents susceptibility of the reaction to solvent ionizing power Y, and is unity for *tert*–butyl chloride solvolysis at 25°C. It was assumed that the rate determinig step of the solvolysis of *tert*–butyl chloride in hydroxylic solvent is the heterolysis of C-Cl bond in the S_N1 process and is not sensitive to solvent nucleophilicity[1]. However Bentley *et al*[8]. argued that comparison of solvolysis rates for 1– or 2–adamantyl compounds with those for *tert*–butyl halides shows involvement of solvent nucleophilicity in *tert*–butyl halides solvolysis. Swain *et al*[9]., have also reported that solvolysis of *tert*–butyl halides are influenced by the solvent nucleophilicity.

In this respect adamantyl derivatives are to be preferred to *tert*–butyl halides in the determination of solvent ionizing power Y[8,10–17]. Adamantyl compounds have rigid, caged structure and rear-side nucleophilic attack is impossible sterically so that a limiting S_N1 mechanism is assured for the solvolysis[10–11]. The adamantyl derivatives used in determination of *Y* values are halides (bromide and chloride)[8,11], *p*–toluenesulfonate (tosylate)[12], perchlorate[13–14] and picrate[15]; those with leaving group of chloroformate[16] and azoxytosylate[17] have also been used. The *Y* values determined based on *tert*–butyl halides and 1– or 2–adamantyl derivatives were mostly for aqueous solutions; those for organic binaries were methanol-acetone mixtures using 2–adamantyl perchlorate[13], methanol-tetramethylene sulfone and ethanol–chloroform mixtures using 1–adamantyl picrate and –tosylate[15].

In this work we have carried out solvolysis of 1–adamantyl chloride, –bromide and –tosylate in isodielectric solvent system of methanol-acetonitrile mixtures, (I). We have then discussed the virtues of the *Y* values thus derived in comparison to the *Y* values based on *tert*–butyl systems.



(I)

Experimental

Methanol and acetonitrile were distilled by the literature methods[18]. 1–Adamantyl chloride and bromide were recrystallized from methanol at –70°C[11]. 1–Adamantyl tosylate was prepared as follows: 4.3 g (0.02*M*) of 1–adamantyl bromide and 6.1 g (0.025 *M*) of silver *p*–toluenesulfonate were left to react for 10 hours at 50°C and silver bromide was removed by filtration. The reaction mixture was then distilled under reduced pressure to obtain white crystal which was recrystallized twice from ether. The m.p (73–79°C) and IR spectra agreed with the literature values[12]. The solvolysis rates of 1–adamantyl chloride and –bromide were determined titrimetrically using Pyrex sealed ampoule technique[19]. The initial substrate concentration was ~0.023 M, and HCl and HBr formed by solvolysis were titrated using standard methanolic NaOMe solution with phenolphthalein indicator. The rate constants were obtained from the slope of linear plots of log $[(\text{titer})_{t=\infty}$—$(\text{titer})_t]$ *vs* time. All rate constants are the averages of duplicate runs. The rate measurements for 1–adamantyl tosylate were carried out conductometrically using Beckmann Model RC–18A conductometer. Temperature was kept constant to within ± 0.05°C and rate constants were determined by the Guggenheim method[20]. The rate constants reported for 1–adamantyl tosylate are the averages of 2–4 kinetic runs.

Results and Disucssion

Solvolysis rate constants for 1–adamantyl chloride, –bromide and –tosylate in methanol–acetonitrile mixtures are summarized in Table 1. In Table 2, *Y* values for adamantyl derivatives determined by equation (1) are given together with $Y_{t\text{-BuBr}}$ and ratios of the rate constants, $k_{t\text{-BuBr}}/k_{1\text{-AdBr}}$ and $k_{1\text{-AdOTs}}/k_{1\text{-AdBr}}$.

TABLE 1: First–Order Rate Constants and Activation Parameters for Solvolysis of 1–Adamantyl Derivatives in Methanol–Acetonitrile Mixtures

Compd	Solvent^c	Temp. °C	k_1, s^{-1}	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ eu
1–AdCl^a	90 MeOH	89.1	$(18.5 \pm 0.1) \times 10^{-7}$	19.6	−26.0
		73.5	$(5.22 \pm 0.05) \times 10^{-7}$		
		25.0^d	4.36×10^{-9}		
	80 MeOH	89.1	$(19.9 \pm 0.3) \times 10^{-7}$	20.4	−23.5
		73.5	$(5.37 \pm 0.12) \times 10^{-7}$		
		25.0^d	3.79×10^{-9}		
	70 MeOH	89.1	$(17.0 \pm 0.1) \times 10^{-7}$	20.5	−23.4
		73.5	$(4.55 \pm 0.04) \times 10^{-7}$		
		25.0^d	3.11×10^{-9}		
	50 MeOH	89.1	$(9.40 \pm 0.10) \times 10^{-7}$	21.5	−21.2
		73.5	$(2.72 \pm 0.06) \times 10^{-7}$		
		25.0^d	2.50×10^{-9}		
1–AdBr^a	100 MeOH	55.0	$(15.8 \pm 0.6) \times 10^{-7}$	18.0	−26.8
		43.0	$(5.35 \pm 0.20) \times 10^{-7}$		
		25.0^d	2.44 ± 10^{-8}		
		25.0^e	2.1×10^{-8}		
	90 MeOH	55.0	$(17.4 \pm 0.2) \times 10^{-7}$	17.6	−28.1
		43.0	$(6.05 \times 0.15) \times 10^{-7}$		
		25.0^d	2.89×10^{-8}		
	80 MeOH	55.0	$(18.0 \pm 0.1) \times 10^{-7}$	17.1	−29.4
		43.0	$(6.41 \pm 0.10) \times 10^{-7}$		
		25.0^d	3.19×10^{-8}		
	70 MeOH	55.0	$(17.3 \pm 0.2) \times 10^{-7}$	17.3	−28.9
		43.0	$(6.10 \pm 0.18) \times 10^{-7}$		
		25.0^d	2.98×10^{-8}		
	50 MeOH	55.0	$(13.7 \pm 0.5) \times 10^{-7}$	17.4	−29.0
		43.0	$(4.80 \pm 0.09) \times 10^{-7}$		
		25.0^d	2.32×10^{-8}		
	30 MeOH	55.0	$(8.55 \pm 0.23) \times 10^{-7}$		
		25.0^f	1.5×10^{-8}		
1–AdOTs^b	100 MeOH	35.0	$(18.8 \pm 0.1) \times 10^{-4}$	21.7	−0.5
		25.0	$(5.53 \pm 0.01) \times 10^{-4}$		
		25.0^g	4.8×10^{-4}		
	90 MeOH	35.0	$(19.4 \pm 0.2) \times 10^{-4}$	21.3	−1.8
		25.0	$(5.84 \pm 0.01) \times 10^{-4}$		
	80 MeOH	35.0	$(18.1 \pm 0.1) \times 10^{-4}$	20.6	−4.2
		25.0	$(5.66 \pm 0.02) \times 10^{-4}$		
	70 MeOH	35.0	$(16.5 \pm 0.2) \times 10^{-4}$	20.5	−4.8
		25.0	$(5.20 \pm 0.01) \times 10^{-4}$		
	50 MeOH	35.0	$(10.8 \pm 0.1) \times 10^{-4}$	19.6	−8.7
		25.0	$(3.58 \pm 0.01) \times 10^{-4}$		
	30 MeOH	45.1	$(16.3 \pm 0.3) \times 10^{-4}$	20.6	−4.2
		35.0	$(5.26 \pm 0.02) \times 10^{-4}$		
		25.0^d	1.65×10^{-4}		

[a] Determined titrimertically in duplicate; errors shown are average deviations. [b] Determined conductometrically in duplicate or quadruplicate; errors shown are average deviations. [c] Volume percent of methanol. [d] Calculated values from data at other temperatures. [e] Reference 8. [f] Extrapolated values of data points for 100–50v/v% methanol–acetonitrile mixtures. [g] Reference 12.

The solvolysis rate constants of 1–adamantyl bromide in methanol–acetonitrile mixtures show a maximum at 80 % methanol. This type of maximum behavior has also been observed for the solvolysis of 2–adamantyl perchlorate in methanol–acetone mixtures,[13] for 1–adamantyl picrate solvolysis in methanol–tetramethylene sulfone mixtures and

TABLE 2: First-Oder Rate Constants of *tert*-Butyl and Adamantyl Derivatives in Methanol-Acetonitrile Mixtures at 25°C and Various Y Scales and Rate Ratios.

Compd	$k_1 \times 10^7$						
	100 MeOH	90 MeOH	80 MeOH	70 MeOH	50 MeOH	30 MeOH	80 EtOH
tert-Butyl bromide[a]	365	439	475	492	422	326	3580[c]
1-Adamantyl chloride[b]		0.0436	0.0379	0.0311	0.0250		0.091[d]
1-Adamantyl bromide[b]	0.244	0.289	0.319	0.298	0.232	0.150	2.8[d]
1-Adamantyl tosylate[b]	5530	5840	5660	5200	5380	1650	40300[e]
Y_{t-BuBr}	−0.992	−0.911	−0.877	−0.862	−0.929	−1.041	0.00
Y_{1-AdCl}		−0.320	−0.380	−0.467	−0.561		0.00
Y_{1-AdBr}	−1.060	−0.986	−0.943	−0.973	−1.082	−1.271	0.00
$Y_{1-AdOTs}$	−0.863	−0.839	−0.852	−0.889	−1.051	−1.388	0.00
k_{t-BuBr}/k_{1-AdBr}	1500	1500	1500	1650	1800	2200	1300
$k_{1-AdOTs}/k_{1-AdBr}$	22600	20200	17700	17400	15400	11000	14400

[a]Reference 7. [b]This work. [c]Reference 3. [d]Reference 8. [e]Reference 12.

for 1-adamantyl tosylate solvolysis in ethanol-chloroform mixtures[15].

Recently Lee *et al*[7]. have shown that the rate constants of *tert*-butyl halides solvolysis in methanol-acetonitrile mixtures exhibit maximum behavior at different solvent compositions depending on the leaving group halides. They interpreted the rate maximum as the result of the cooperative enhancement of rate by polarity (π^*)[21] and hydrogen bond donating (HBD) ability (α)[21] of the solvent. The polarity increases with the acetonitrile content while HBD ability increases with the methanol content of the solvent mixtures. The combined effect of the two on the solvolysis rate becomes maximum at the optimum composition where the importance of the two effect differs depending on the leaving group; for chloride HBD ability is more important whereas for iodide the polarity effect becomes increasing important so that the maximum shifts from 90 % to 50 % methanol as the leaving group is changed from chloride to iodide. For bromide the maximum appeared at 80% methanol solution.

It has been shown that Swain's cation solvating power B can be linearly correlated with the polarity parameter π^* of Taft *et al.*, while anion solvating power A measures a blend of about 30 % solvent polarity and 70 % hydrogen bond donor ability[22]. Our determinations of A and B values for methanol-acetonitrile mixtures have indeed supported the contention; A increased with methanol content (as HBD ability, α, does) while B increased with acetonitrile content (as polarity, π^*, does) of the solvent mixtures[23].

On the other hand in a recent theoretical studies on water chain involvement in solvolysis mechanism, Bertrán *et al*[24]., have shown that in the hydrolysis of methyl fluoride, four water molecules participate in a push-pull chain. They have argued that there is a solvent assistance in the ionizing process by stabilizing incipient cation and/or anion.

In view of the results of these studies, one may rationalize the position of the maximum with cation and anion solvation tendencies of the mixed solvent. Thus we may attribute the shift of the rate maximum toward higher methanol content for *tert*-butyl chloride with respect to iodide to increasing importance of anion solvation.

For adamantyl series investigated in this work the rate maxima appear at approximately the same compositions with those for *tert*-butyl series; for bromide at 80 % methanol and for chloride most probably at 90 % methanol although we were not able to obtain the rate constant at 100 % methanol due to the experimental difficulties.

Interestingly, tosylate had the maximum at 90 % methanol indicating strong influence of HBD ability (α) or anion solvating power, A. This may be due to the stabilizing interaction of sulfonate oxy-anion by HBD power of methanol. Reference to Table 2 reveals that when cation is varied from 1-adamantyl to *tert*-butyl keeping the anion constant to bromide, the rate ratio k_{t-BuBr}/k_{1-AdBr} increases with the acetonitrile content of the solvent, and hence cation solvating power B of the solvent, in agreement with the greater cation solvation expected of *tert*-butyl cation compared to 1-adamantyl cation. Within 80–100 % methanol region, the cation solvating power of the mixture may be small enough so that the difference in cation solvation becomes negligible and the rate ratio remains constant.

On the other hand if we change the leaving group from bromide to tosylate keeping the cation constant to 1-adamantyl, the rate ratio $k_{1-AdOTs}/k_{1-AdBr}$ increases with methanol content, and hence with anion solvating power A. This clearly demonstrates the importance of anion solvation for tosylate.

Various Y values given in Table 2 show that Y values based on 1-adamantyl tosylate have largest variation for the same composition change of the solvent mixture: from 30–100 % methanol, Y_{t-BuBr}, Y_{1-AdBr} and $Y_{1-AdOTs}$ vary 0.049, 0.211 and 0.525 unit respectively. We therefore think that the $Y_{1-AdOTs}$ scale is much superior to other solvent ionizing power scales and agree with Bentley[25] in adopting Y_{OTs} as a better choice for solvent ionizing power scale, especially for the weakly ionizing medium, *i.e.*, $Y<O$. Plots of Y_{t-BuBr} against Y_{1-AdBr} are given in Figure 1. The enhanced cation solvation of *tert*-butyl bromide relative to 1-adamantyl bromide is shown by the upper line connecting Y values for 30–70 % methanol mixtures. Exactly opposite situation holds for Y_{1-AdOT} vs Y_{1-AdBr} plots in Figure 2. The upper

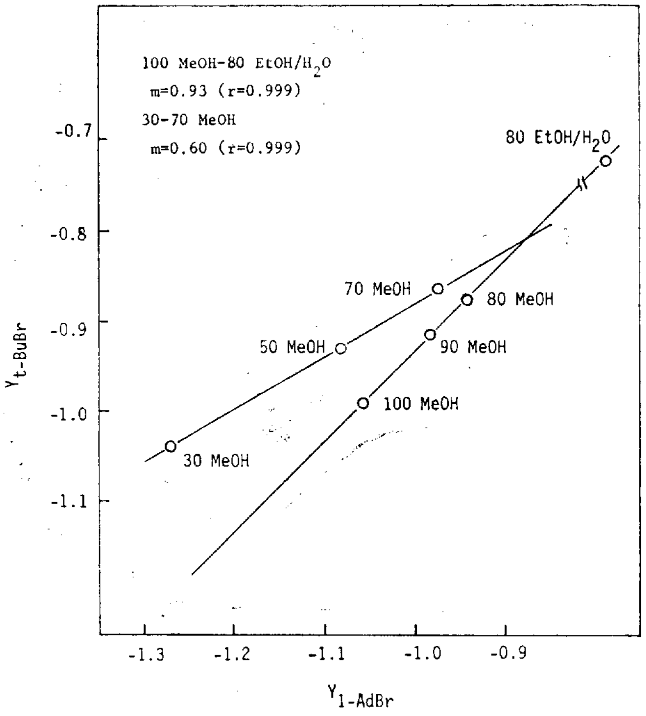


Figure 1. Plots of $Y_{1\text{-AdBr}}$ *vs.* $Y_{t\text{-BuBr}}$ in methanol-acetonitrile mixtures at 25°C.

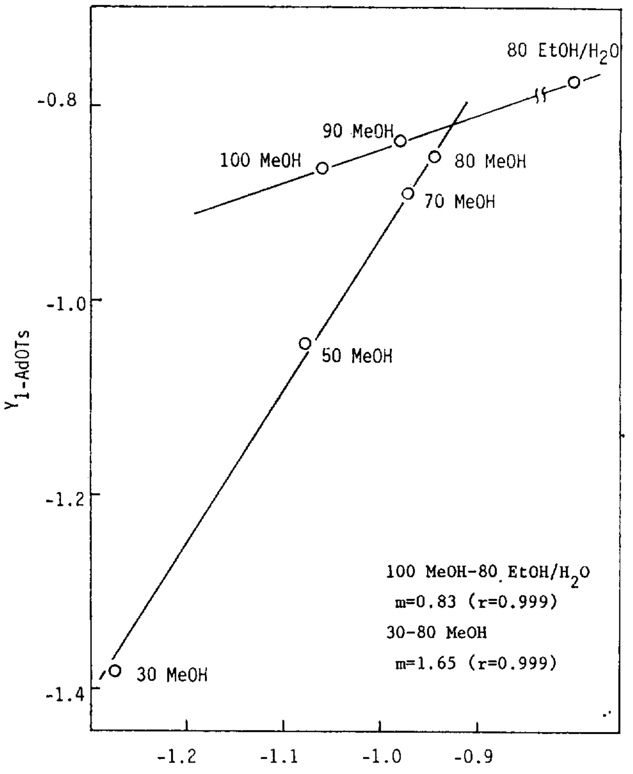


Figure 2. Plots of $Y_{1\text{-AdBr}}$ *vs.* $Y_{1\text{-AdOTs}}$ in methanol-acetonitrile mixtures at 25°C.

straight line is a clear indication of enhanced anion solvation for tosylate. The largest slope of 1.65 for 30-80 % methanol region obtained in Figure 2 shows again the large variation of $Y_{1\text{-AdOTs}}$ relative to $Y_{1\text{-AdBr}}$

Entropies of activation in Table 1 for 1-adamantyl tosylate solvolysis in methanol-acetonitrile mixtures are small and negative($-0.5\sim-8.7$ e.u.), characteristic of a modest solvent reorganization accompanying activation process; this shows that in the activation process, tosylate anion has very little reorganization of solvent structure around it since in the ground state solvation of oxy-anion is already sizable. Moreover adamantyl cation will also have very little solvation due to sterically inhibiting cage structure of the adamantyl skeleton.

We therefore conclude that: (i) The rate maximum observed is a result of cooperative enhancement of cation and anion solvation at the optimum composition of solvent mixture depending on the nature of cation and/or anion. (ii) Adamantyl tosylate has small cation solvation but has extensive anion solvation. (iii) *Y* scale based on adamantyl tosylate is superior to other *Y* scales since it varies in a wide range especially for weakly ionizing medium.

Acknowledgement. We thank the Korea Science and Engineering Foundation for support of this work.

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Charge-Transfer Complexing Properties of 1-Methyl Nicotinamide and Adenine in Relation to the Intramolecular Interaction in Nicotinamide Adenine Dinucleotide (NAD$^+$)

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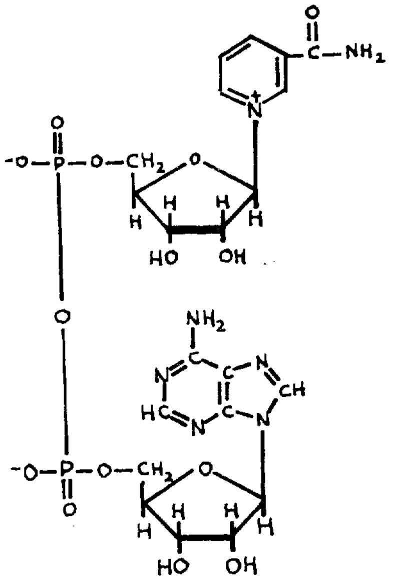
The charge-transfer complexing properties of 1-methyl nicotinamide (MNA), an acceptor, and adenine, a donor, were investigated in water and SDS micellar solutions in relation to the intramolecular interaction in nicotinamide adenine dinucleotide (NAD$^+$). The spectral and thermodynamic parameters of MNA-indole and methyl viologen-adenine complex formations were determined, and the data were utilized to evaluate the charge-transfer abilities of MNA and adenine. The electron affinity of nicotinamide was estimated to be 0.28 eV from charge-transfer energy of ~300 nm for MNA-indole. The large enhancement of MNA-indole complexation in SDS solutions by entropy effect was attributed to hydrophobic nature of indole. The complex between adenine and methyl viologen showed an absorption band peaked near 360 nm. The ionization potential of adenine was evaluated to be 8.28 eV from this .The much smaller enhancement of charge-transfer interaction involvinga denine than that of indole in SDS solutions was attributed to weaker hydrophobic nature of the donor. The charge-transfer energy of 4.41 eV (280 nm) was estimated for nicotinamide-adenine complex. The spectral behaviors of NAD$^+$ were accounated to the presence of intramolecular interaction in NAD$^+$, which is only slightly enhanced in SDS solutions .The replacement of nicotinamide-adenine interaction in NAD$^+$ by intermolecular nicotinamide-indole interaction in enzyme bound NAD$^+$, and guiding role of adenine moiety in NAD$^+$ were discussed.

Introduction

The coenzyme nicotinamide adenine dinucleotide (NAD$^+$; I) is a major electron acceptor in all known forms of life. Its function as electron acceptor in enzymatic oxidation-reduction reactions necessitates some type of enzyme-coenzyme interactions in which NAD$^+$ acts through the reversible reduction of its nicotinamide moiety.

In 1956, Kosower[1] ascribed the moderately intense long wavelength absorption band appearing in the mixtures of NAD$^+$ and glyceraldehyde-3-phosphate dehydrogenase (GPD) to a charge-transfer band from a donor to the pyridine cation of NAD$^+$. Cilento and Guisti[2] found that tryptophan gave rise to charge-transfer band with 1-benzyl nicotinamide, which was similar in both contour and intensity to the spectrum of GPD in the presence of NAD$^+$. Extensive studies on charge-transfer complex formation between NAD$^+$ or its model compounds and indole derivatives in homogeneous solutions[1-4], and in the presence of micelle[5], vesicle[6], and polyelectrolyte[7] have been followed.

Besides nicotinamide moiety, NAD$^+$ bears an adenine moiety, which can act as an electron donor. The intramolecular interaction between nicotinamide and adenine moieties in NAD$^+$ is possible and the interaction, if any, would affect coenzyme activity of NAD$^+$. In fact, the charge-transfer interaction between 1-substituted nicotinamide and adenine



I. NAD$^+$