Solvent Effects on the Solvolysis of 2-Aryl-1,1-dimethylethyl Bromides

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Solvolysis rates of substituted 2-aryl-1,1-dimethylethyl bromides (**1**) were determined in a variety of solvents such as aqueous mixtures of ethanol, acetone, 2,2,2-trifluoroethanol, and also mixtures of ethanol and TFE at 25 °C, 35 °C, and 45 °C. The solvent effects were analyzed in terms of Winstein-Grunwald equation. The solvent effects of 1-4-MeO failed to give a single linear correlation against either Y or Y_{Cl} (Y_{Br}), but exhibited a wide split pattern which could not be related to the solvent nucleophilicity. On the other hand 1-4-CH$_3$ and 1-H gave a fairly good linearity. In the case of **1-4-MeO**, a fairly good linearity was observed against Y_{Δ} defined from the solvolysis of 4-methoxyneophyl tosylate. It is assumed that resonance interaction between reaction site and aryl-π-system operates to give charge delocalization regardless of the different solvolysis mechanisms. The Hammett-Brown treatment of the solvolytic rate constant of compounds **1** was obtained non-linear two separated lines of −1.06 to −1.46, suggesting of mechanistic changeover from k_c-k_s to k_{Δ} on going from electron-withdrawing to electron-donating substituents as a basis of 4-CH$_3$ group.

Introduction

In the previous papers,[1] we have treated the substituent effects on the solvolysis of 1-(4-methoxyphenyl)-1-phenyl-2,2,2-trifluoroethyl chlorides (**2**) based on the Yukawa-Tsuno equation[2] in 80% aqueous ethanol. The results suggested that the carbocationic charge in the transition state was dispersed mostly by *p*-methoxy group. Since solvent acts as both medium and reagent in the solvolysis reaction,[3] the solvolysis rate is affected by both polarity and nucleophilicity of the solvent. Therefore, another approach to investigate the solvolysis mechanism is to apply solvent effect correlation analysis. The solvolyses of **2** gave improved correlations with Y_{BnCl}[4] and extended dual-parameter treatment $\log k/k_o = mY_{Cl} + hI$ ($m_{\Delta}Y_{\Delta}$)[5] in a variety of aqueous binary solvents, indicating the incipient cationic charge is delocalized strongly on the aryl-rings in the transition state. While 1-(4-methoxyphenyl)-1-phenylethyl chloride (**3**) was better correlated with the extended Grunwald-Winstein equation,[6,7] $\log (k/k_o) = mY_{Cl} + lN_{OTs}$, indicating the cationic charge of reaction center of **3** is localized mostly in the transition state.

Winstein and Grunwald proposed the ionizing power scale, Y, based on the solvolysis of t-butyl chloride in a variety of solvents by Eq. (1),[6]

$$Y = \log (k/k_{80E})_{t\text{-BuCl}} \tag{1}$$

and proposed an empirical linear free energy relationship, Eq. (2)

$$\log (k/k_{80E}) = mY \tag{2}$$

where *k* is rate constant in any solvent, and *m* is a sensitivity of each substrate to solvent ionizing power Y. Schleyer and Bentley proposed to the preferred use of 2-adamantyl tosylate as a standard substrate instead of *t*-butyl chloride and defined Y_{OTs} scale for tosylate solvolysis,[7]

$$\log (k/k_{80E}) = mY_{OTs} \tag{3}$$

and they further defined a solvent nucleophilicity N_{OTs} using the solvolysis rates of methyl tosylate. To evaluate the character of the transition state in nucleophilically assisted solvolyses of primary and secondary alkyl tosylates, the extended Grunwald-Winstein Eq. (4) can be used.

$$\log (k/k_{80E}) = mY_{OTs} + lN_{OTs} \tag{4}$$

where N_{OTs} is drived from the solvolysis of methyl tosylate, as an extreme of S_N2 solvolysis using Eq. (5),

$$N_{OTs} = \log (k/k_{80E})_{MeOTs} - 0.3Y_{OTs} \tag{5}$$

The solvent effect on solvolyses of various 2-arylalkyl tosylates in a wide variety of solvent based on Eq. (4) was studied, but the solvent effect on benzylic k_{Δ} and aryl-assisted k_{Δ} solvolysis failed to give a single linear correlation with the 2-adamantyl Y_{OTs} parameter.[8]

Recently Fujio and Tsuno proposed to use the solvolysis of 4-methoxyneophyl tosylate as a standard for the solvent polarity scale for the solvolysis where charge delocalization in the transition state operates such as β-arylalkyl k_{Δ} and benzylic k_c solvolysis by Eq. (6),[8]

$$Y_{\Delta} = \log (k/k_{80E})_{4\text{-meothoxyneophyl OTs}}$$
$$\log (k/k_{80E}) = m_c Y_{OTs} + m_{\Delta} Y_{\Delta} \tag{6}$$

using two extremes for the localized cation of 2-adamantyl Y_{OTs} and delocalized cation of 4-methoxyneophyl Y_{Δ} employed as the solvent polarity scale. The solvolysis of neophyl brosylates (2-methyl-2-phenylpropyl *p*-bromobenzenesulfonate) has often used as a reference set of the substituent effects on β-aryl assisted solvolysis. The importance of neighboring phenyl participation can be estimated from the effects of aryl substituents which have therefore been an important tool for the reaction mechanism.

From the similarity in structure between 2-aryl-1,1-dimethylethyl bromide and neophyl brosylate, we can expect a close similarity in the reaction mechanism between the two systems. In this paper, we have concerned quantitative explanation of the dispersion pattern of solvent effect on the solvolysis of 2-aryl-1,1-dimethyl bromides. The kinetic data

obtained from the solvent effect analysis will provide us important information of estimating the transition state structure of solvolysis.
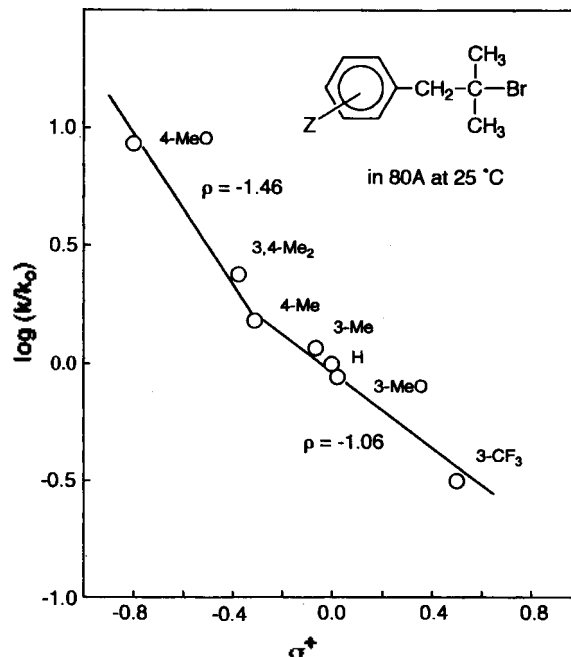
Results and Discussion

Substituent effect on the solvolysis of 2-aryl-1,1-dimethylethyl bromides. Solvolysis rates of substituted 2-aryl-1,1-dimethylethyl bromides (1) were determined in solvents such as aqueous acetone and ethanol. First order rate constants and some activation parameters for the solvolysis of 1 are listed in Table 1, and logarithmic rates of compounds 1 are plotted against Hammett σ (σ^+) in Figure 1. As shown in Table 1, the electron-donating substituents facilitate the reaction, indicating the positive charge development at the reaction center of the α-carbon. Aqueous ethanols are much stronger nucleophilic solvent than aqueous acetones. As a consequence, solvolysis reactions proceeding with nucleophilic solvent assistance in aqueous ethanols show larger rate constants than that in aqueous acetones, since the large hydrogen bonding effects in aqueous ethanols stabilize the transition state in the solvolysis reaction.

The Hammett-Brown treatment of the solvolytic rate constant of compounds 1 in 80% aqueous acetone displays a non-linear correlation as shown in Figure 1, which indicates that there is a change in the reaction mechanism. The two separated lines (ρ value of -1.06 to -1.46) of the Hammett plot are suggestive of mechanistic changeover from k_c-k_s to k_Δ on going from electron-withdrawing to electron-donating substituents as a basis 4-CH$_3$ group. The logarithmic rate constant plot of 80E *vs.* 80A for the whole substituent range gives a linear correlation as shown in Figure 2. This suggests that solvolytic mechanism of 1 does not vary with the change of same percent of aqueous ethanol and aqueous acetone.

Solvent effect on the solvolysis of 2-aryl-1,1-dimethylethyl bromides. Solvolysis rates of 1 were determined in a variety of solvents using an electroconductimetric method. The range of solvents covers aqueous binary mixtures of ethanol, acetone, and 2,2,2-trifluoroethanol (TFE), and also includes ethanol-TFE mixtures. The kinetic
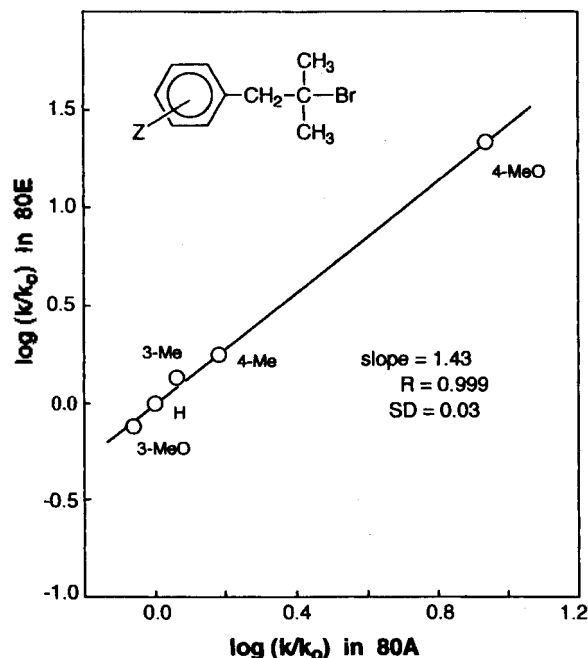

Figure 1. Substituent effect on the solvolysis of 2-aryl-1,1-dimethylethyl bromides in 80% aqueous acetone at 25 °C.

results and various solvents parameters are listed in Table 2, in which the electron-donating substituents increased the rate as already mentioned. In Figure 3, logarithmic rate constants for the solvolysis of 1 at 25 °C are plotted against Y values based on the solvolysis of tert-butyl chloride using Eq. 2, giving m=0.80 with a fairly good correlation coefficient (R=0.995 and SD=±0.02) in the case of unsubstituted compound of 1. However electron-donating substituents

Table 1. Rate Constants (10^5 k_1, s^{-1}) for the Solvolysis of 2-Aryl-1,1-dimethylethyl Bromides in 80% aqueous acetone and 80% aqueous ethanol

|	Temp. (°C)	80A	80E	$\Delta H^{\ddagger}_{25}$ °C (kcal/mol)	$\Delta H^{\ddagger}_{25}$ °C (e.ul)
4-MeO	25	16.4	126		
	35	78.0		19.5	-9.8
	45	168			
3,4-Me$_2$	25	4.57			
4-Me	25	2.90	10.3		
3-Me	25	2.21	7.59		
H	25	1.91	5.79		
3-MeO	25	1.66	4.41		
	35	5.01		19.2	-16
	45	13.5			
3-CF$_3$	25	0.60			

Figure 2. Linear logarithmic rate relation for the solvolysis of 2-aryl-1,1-dimethylethyl bromides between 80% aqueous acetone and 80% aqueous ethanol at 25 °C.

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Table 2. Rate Constants (10^5 k_1, s^{-1}) for the Solvolysis of 2-Aryl-1,1-dimethylethyl Bromides at 25 °C

	H	4-CH3	4-CH3O	Y^b	Y_{Br}^c	Y_Δ^d
80A	1.91	2.90	16.4	-0.67	0.70	-0.82
70A	8.61	9.43	77.9	0.13	0.20	-0.45
60A	27.4	30.4	310	0.80	1.03	-0.12
50A	84.7	89.8	725	1.40	1.74	0.20
40A		307		1.98	2.44	0.55
80E	5.79	10.3	121	0.00	0.00	0.00
70E	18.3	23.7	474	0.60	0.68	0.22
60E	48.9	45.6	1263	1.12	1.26	0.39
50E	108	200		1.66	1.88	0.61
40E		319		2.20	2.62	0.83
80ET	0.503	0.887	43.1	-1.52		-0.39
60ET	1.62	2.21	89.9	-0.87		0.02
40ET	3.54	4.12	474	-0.27		0.43
20ET		16.4	1021	0.41		0.82
98Tw	71.0	112		1.15	2.53	1.12
80T	120	170		1.35		1.09
70Tw	181	234		1.66	2.79	1.07
50Tw		237		1.96	3.04	1.09
50T		228				1.08

^{a} Volume percent of first-named organic component, unless otherwise noted. Abbreviation, E=ethanol, A=acetone, T=TFE=2,2,2-trifluoroethanol, ET=ethanol-TFE mixtures (e.g., 20ET=20 vol EtOH: 80 vol TFE mixture). suffix w means weight percent. ^{b} Y= log(k/k_o) for the solvolysis of t-butyl chloride at 25 °C. $^c Y_{Br}$=log (k/k_o) for the solvolysis of 1-adamantyl bromide at 25 °C. $^d Y_\Delta$= log(k/k_o) for the solvolysis of 4-methoxyneophyl tosylate at 45 °C.
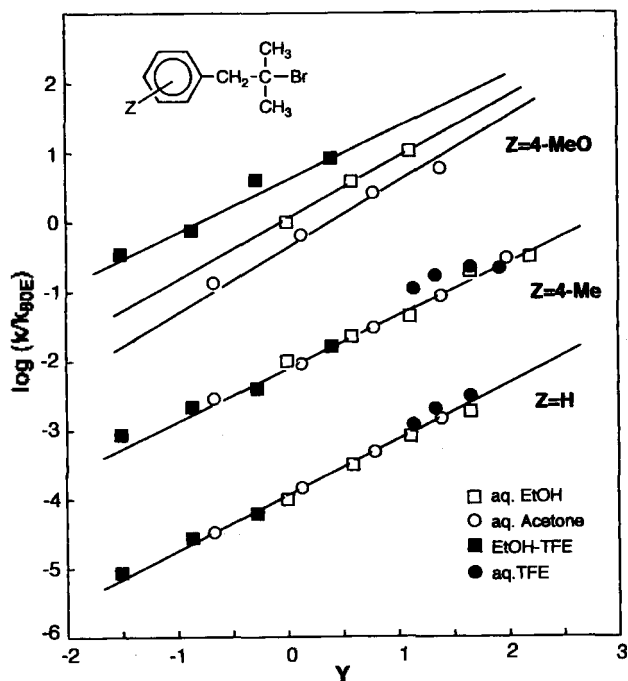
Figure 3. The mY plots of the solvolysis of 2-aryl-1,1-dimethylethyl bromides at 25 °C. Offset by -2 from above y-axis.

Table 3. Correlation Analysis of Solvents Effects on Solvolysis of 1 according to Grunwald-Winstein equation; log (k/k_o)=mY_x (+lN_{OTs})

	Y_x	m	l	R^a	n^b
p-CH3O	Y	0.54±0.14		0.777	11
		0.55±0.13	-0.40±0.23	0.843	11
	Y_{Cl}	0.52±0.08		0.915	11
		0.53±0.09	0.05±0.19	0.915	11
p-CH3	Y	0.74±0.03		0.986	18
		0.73±0.03	-0.11±0.04	0.991	18
	Y_{Cl}	0.54±0.05		0.948	18
		0.62±0.04	0.29±0.07	0.977	18
H	Y	0.80±0.02		0.995	14
		0.78±0.02	-0.08±0.02	0.998	14
	Y_{Cl}	0.55±0.05		0.951	14
		0.66±0.04	0.32±0.07	0.985	14

^{a} Correlation coefficient. ^{b} Number of data points involved.

Table 4. Correlation Analysis of Solvents Effects on Solvolysis of 1 according to Grunwald-Winstein equation; log (k/k_o)=mY_x+ $m_\Delta Y_\Delta$(+lN_{OTs})

	Y_x	m	m_Δ	l	R^a	n^a
p-CH3O	Y	0.30±0.05	0.91±0.10		0.982	11
		0.28±0.06	0.98±0.13	0.09±0.11	0.983	11
	Y_{Cl}	0.31±0.08	0.65±0.18		0.968	11
		0.29±0.06	0.82±0.14	0.26±0.09	0.985	11
p-CH3	Y	0.68±0.04	0.15±0.08		0.989	18
		0.73±0.05	0.00±0.11	-0.11±0.06	0.991	18
	Y_{Cl}	0.79±0.08	-0.68±0.02		0.970	18
		0.75±0.07	-0.41±0.18	0.22±0.07	0.983	18
H	Y	0.75±0.03	0.11±0.05		0.996	14
		0.77±0.03	0.02±0.06	-0.07±0.03	0.998	14
	Y_{Cl}	0.80±0.09	-0.66±0.21		0.975	14
		0.80±0.05	-0.42±0.12	0.26±0.05	0.993	14

^{a} See footnotes a and b of Table 3.

such as p-methyl and p-methoxy groups did not show a good correlation but exhibited a widely split pattern for binary solvent series in the p-methoxy as shown correlation coefficient (R=0.777 and SD=±0.14). Especially, the plots

for less nucleophilic solvents such as aqueous TFE and ethanol-TFE mixtures lie above the one for the aqueous ethanol and acetone series. Plots for aq ethanol series lie above those for aq acetone series. Obviously, the deviation patterns from the mY correlation are not consistent with what would be anticipated for a mechanistic involvement of the solvent nucleophilicity.

Results of solvent effect analysis by extended Grunwald-Winstein equation are shown in Tables 3 and 4. The m values for all solvents are ca 0.8 for 1-H, 0.7 for 1-p-CH3, and 0.5 for 1-p-MeO. The strong π-donor system, 1-p-MeO, gave poor correlation (R=0.777-0.915). On the other hand, 1-p-CH3 and 1-H gave a fairly good linearity against Y and Y_{Cl}[10] (R=0.948-0.998).

The smaller m value for more reactive substrate is not in line with the involvement of solvent nucleophilicity and therefore the reduced charge due to internal delocalization[8,11-12] must result in the reduced sensitivity to solvent ionizing power. In Figure 4, downward deviation of aq. TFE from the correlation line of aq. ethanol and aq. acetone in the 1-p-CH3 with the Y_{Br} plot is suggesting the more contribution of solvent nucleophilicity than 1-adamantyl bromide in solvolysis reaction. Downward deviations of less nu-
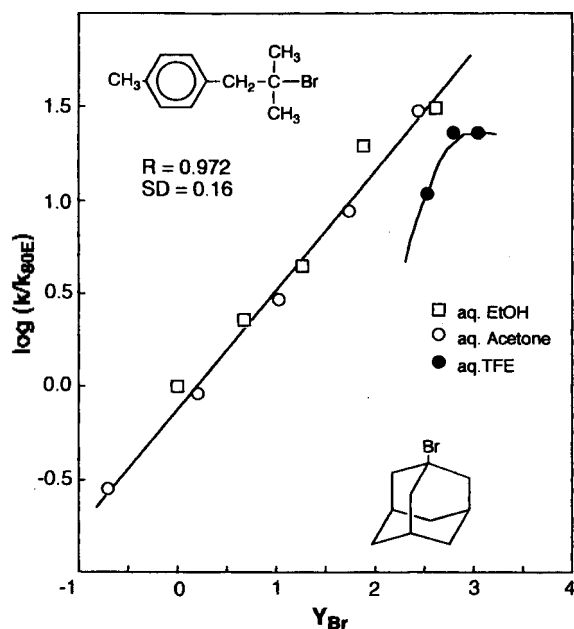
Figure 4. The mY_{Br} plot of the solvolysis of 2-(4-methylphenyl)-1,1-dimethylethyl bromides at 25 °C.

cleophilic solvents were reasonably described by the additional lN_{OTs} term by Eq. 4, log $(k/k_o)_{l-p-Me}=0.62Y_{Br}+0.19N_{OTs}$ (R=0.993, SD=0.09), as shown Figure 5. Increased contribution of lN_{OTs} term is evaluated from -0.4 to -0.1 by Y scales and 0.1 to 0.3 by Y_{Cl} scales covering the p-MeO to unsubstituted H, which means the nucleophilicity of solvent increases in this order as shown in Table 3. However, it is demonstrated that the correlation result of 1-p-MeO is not so better than that of 1-p-CH₃ and 1-H. Therefore, it is requested to use the other parameter to correlate this solvent effect.
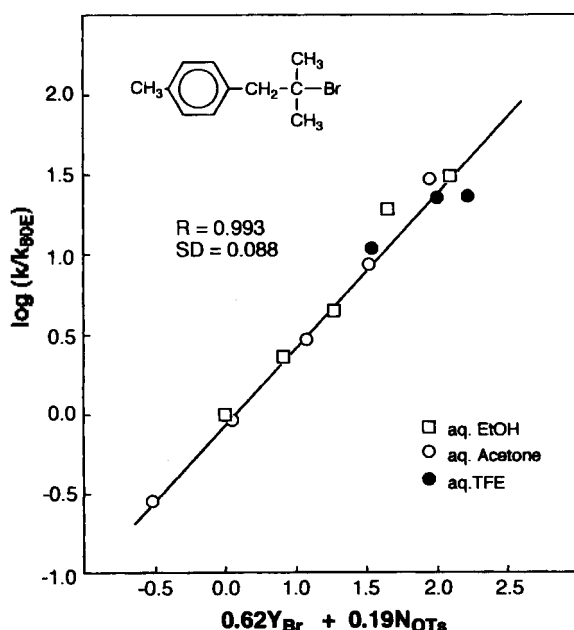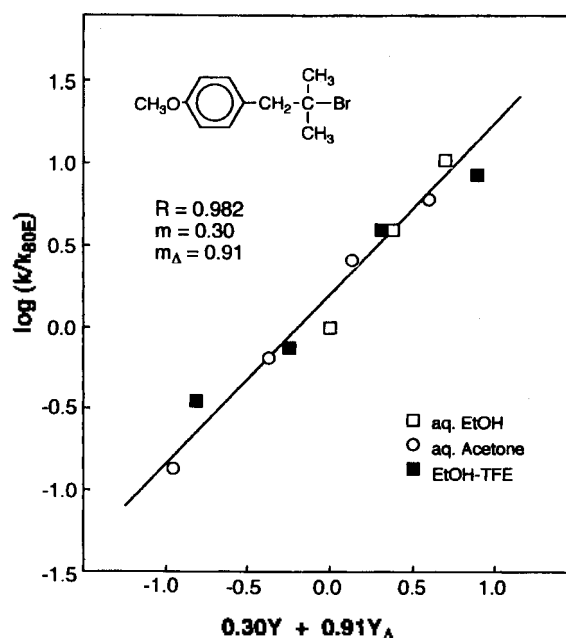
Extensively scattered mY plot for benzylic solvolysis has been reported for the solvolysis system through resonance-stabilized carbocationic transition state such as 1-phenyl, 4-methoxybenzyl and diarylmethyl halides.[12] Reduced *m* value and dispersed mY plot were interpreted in terms of reduced charge at the reaction center due to enhanced stabilization by internal charge delocalization. It has been suggested that the solvent parameter derived from the solvolysis of neophyl derivative is suitable to correlate the solvent effects of benzylic solvolysis.[11] Correlation analysis of the slovent effect on 1-p-MeO using Y_A based on the solvolysis of 4-methoxyneophyl tosylate shows improved linearity, log (k/k_o) $=1.08Y_A+0.22$, with a correlation coefficient, R=0.904, compare to R=0.777 of the Table 3. Solvolysis of 1-H which showed the least scattered solvent effect in mY plot, gives a better correlation result against Y_{Cl} than that of 1-p-MeO. On the other hand, the solvolysis of 1-p-MeO exhibits good dependence on Y_A in spite of most scattered solvent effect in mY plot. This means that there is a significant difference in both the dispersion behavior and the solvent stabilization between 1-H and 1-p-MeO. The dual similarity comparison treatment of the solvent effect of 1 using two extremes, Y_{Cl} and Y_A, is effective to evaluate the extent of k_C and k_A quantitatively,

$$\log (k/k_{80E})=mY_{Cl}+m_AY_A \qquad (7)$$

where 1-adamantyl Y_{Cl} is employed as a parameter for the charge localized cationic solvolysis and 4-methoxyneophyl Y_A is employed as a parameter for the charge delocalized one. Coefficients m and m_A are adjustable blending parameters for Y_{Cl} and Y_A.

Application of Eq. (7) for the solvent effects on the solvolysis of 1-p-MeO does effectively improve the correlation (m=0.30, m_A=0.91, and R=0.982) as shown in Figure 6.

In conclusion, the dispersion behavior of the solvent effect on the solvolysis of 1-p-MeO arise from a π-delocali-

Figure 5. The $(mY_{Br}+lN_{OTs})$ plot of the solvolysis of 2-(4-methylphenyl)-1,1-dimethylethyl bromides at 25 °C.

Figure 6. The $(mY+m_AY_A)$ plot of the solvolysis of 2-(4-methoxyphenyl)-1,1-dimethylethyl bromides at 25 °C.

zation of carbocationic charge in the transition state caused by aryl assistance between aryl ring and the incipient carbocation center, while the carbocationic center of 1-p-Me and 1-H is far from the π-delocalization. It has been demonstrated that the use of Eq. 7 is much effective for the correlation of the solvent effect on the solvolysis of β-arylalkyl systems. It is assumed that charge localized benzylic cation can be correlated by Y_{Cl} and charge delocalized cation can be correlated by Y_A since resonance interaction between reaction site and aryl-π-system operates to give charge delocalization regardless of the different solvolysis mechanisms.

Experimental

General remarks. ^{1}H NMR spectra were recorded on a varian Unity plus-300-MHz spectrometer with TMS as an internal standard. mass spectral analysis was obtained with HP 5890 series 11 GC/5970 instrument. Purities of synthetic materials were investigated with Varian 3300 gas chromatography. For the isolation and identification of synthetic materials were used silicagel and Art 5554 DC-Alufolien kiesegel 60 F_{254} from Merk.

Materials. Organic solvents and water for the kinetic studies were purified as described earlier.[1] The binary mixtures were prepared by mixing the corresponding volumes or weights of the pure solvent at 25 °C. 2-Aryl-1,1-dimethylethanols were prepared by a reaction of the substituted benzyl magnesium bromide and acetone in dry ether. The bromides were prepared by a reaction of the corresponding alcohols and phosphorus tribromide in tetrachloromethane and were purified from a silicagel column. 2-(4-Methoxy phenyl)-1,1-dimethylethyl bromide: oil; ^{1}H NMR (300 MHz, CDCl$_3$); δ 6.80-7.33 (m, 4H, aryl), 3.79 (s, 3H, OCH$_3$), 2.83 (s, 2H, CH$_2$), 1.64 (s, 6H, CH$_3$); MS (EI, m/z) 242 (M$^+$). 2-(4-Methyl phenyl)-1,1-dimethylethyl bromide: oil; ^{1}H NMR (300 MHz, CDCl$_3$); δ 7.12-7.36 (m, 4H, aryl), 3.16 (s, 2H, CH$_2$), 2.34 (s, 3H, CH$_3$), 1.75 (s, 6H, CH$_3$); MS (EI, m/z) 226 (M$^+$). 2-(3-Methyl phenyl)-1,1-dimethylethyl bromide: oil; ^{1}H NMR (300 MHz, CDCl$_3$); δ 6.99-7.34 (m, 4H, aryl), 3.16 (s, 2H, CH$_2$), 2.32 (s, 3H, CH$_3$), 1.74 (s, 6H, CH$_3$); MS (EI, m/z) 226 (M$^+$). 2-Phenyl-1,1-dimethylethyl bromide: oil; ^{1}H NMR (300 MHz, CDCl$_3$); δ 7.16-7.41 (m, 5H, phenyl), 3.19 (s, 2H, CH$_2$), 1.75 (s, 6H, CH$_3$); MS (EI, m/z) 212 (M$^+$). 2-(3-Methoxy phenyl)-1,1-dimethylethyl bromide: oil; ^{1}H NMR (300 MHz, CDCl$_3$); δ 6.71-7.41 (m, 4H, aryl), 3.77 (s, 3H, OCH$_3$), 3.16 (s, 2H, CH$_2$), 1.75 (s, 6H, CH$_3$); MS (EI, m/z) 242 (M$^+$). 2-(3-trifluoromethyl phenyl)-1,1-dimethylethyl bromide: oil; ^{1}H NMR (300 MHz, CDCl$_3$); δ 7.22-7.62 (m, 4H, aryl), 3.20 (s, 2H, CH$_2$), 1.76 (s, 6H, CH$_3$); MS (EI, m/z) 280 (M$^+$).

Kinetic Measurement. Solvolysis rates were measured using an electroconductimetric method.[13] Conductance measurements were made in a 100 cm^3 cell with platinum electrodes using approximately 30 cm^3 solution at an initial concentration of 10^{-3}-10^{-4} mol/L of substrate in a thermostated water bath at appropriate temperature (25, 35, and 45 °C) controlled within ±0.01 °C. Conductivity readings were taken by using a conductivity meter (CM-60S equipped with time interval unit and printer, TOA Electric

Ltd.). All solvolysis reactions were followed by taking about 120 points for three half-lives and an infinity reading was taken after 10 half-lives. The first-order rate constants were determined by least squares computer program and gave excellent first-order behavior with correlation coefficient of greater than 0.9999.

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