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Solvolysis of 1-Aryl-1-tert-butylmethyl Bromides. Hammett-type Correlation Analysis and Revised Y_{BnBr}Scale

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The solvolysis of a series of 1-aryl-1-tert-butylmethyl bromides (1a-1g) in a variety of solvents were carried out. Linear relationships were observed from Hammett-type analysis of logarithm of rate constants using single-parameter Brown-Okamoto equation (Eqn. 1) and dual-parameter Yukawa-Tsuno equation (Eqn. 2), respectively. The p values and the γ values were found to depend mainly on the range of substituents and not the type of solvents employed. The observation of an upward deviation for the data points of strongly deactivating substrates 1f and 1g could be interpreted by an electrophilic acceleration owing to the solvation of leaving group. It is likely an additional example of overshadowed solvent effect in the dual-parameter treatment of rate data. Moreover, the variation of γ values was found contradicting the general consideration of resonance contribution. The observed excellent linear correlations with Y_{BnBr} and the good solubility in aqueous solution with high percentage of water made 1c a better reference standard than 2-bromo-2-(4-trifluormethyl)adamantane (3) for obtaining revised and extended Y_{BnBr} values. Correlation analysis using the single-parameter Grunwald-Winstein equation (Eqn. 3) with Y_{BnBr} was found to be superior over the dual-parameter equation containing Y_{Br} and I (Eqn. 5).

INTRODUCTION

The solvolysis of 1-aryl-1-tert-butylmethyl bromides (1) and chlorides (2) was generally considered to proceed via limiting S_N1 mechanism,¹⁻³ with the exception of 1-tert-1-(4-methoxyphenyl)methyl chloride (2a) in the poorly ionizing acetic acid.⁴ From the study of Hammett-type correlation analysis (Eqns. 1 and 2) for chlorides 2a-2f in different solvents, we found that the function of solvent might be overshadowed and some kind of computational artifact could be introduced in the Yukawa-Tsuno treatment (Eqn. 2).^{3b} To explore whether or not such an observation can be considered as a generalization, an examination on the corresponding bromides is thus desirable.

$$\log(k/k_{\rm o}) = \rho\sigma^{*} \tag{1}$$

$$\log(k/k_{o}) = \rho \left[\sigma^{o} + \gamma (\sigma^{*} - \sigma^{o})\right]$$
⁽²⁾

On the other hand, in our previous study on the solvolysis of benzylic substrates, new scales of solvent ionizing power, Y_{Bnx} ,⁵ were developed for Grunwald-Winstein type correlation analyses (Eqns. 3 and 4). Some preliminary work suggested a few of the original Y_{BnBr} values⁶ were incorrect,⁷ probably due to the poor solubility of the reference standard, 2-bromo-2-(4-trifluoromethyl)phenyladamantane (3) in certain solvents. Since Y_{BoCl} values⁸ for chlorides could be extended from the solvolysis rate data for 1-*tert*butyl-1-(4-methylphenyl)methyl chlorides (2c),^{3a} we are seeking a substitute of 3 to revise and to obtain more Y_{BoBr} values. The similarity of structure between 2c and bromides 1 made the latter a good candidate for such a purpose.

$$\log(k/k_{\rm o}) = mY \tag{3}$$

$$\log(k/k_{\circ}) = mY + lN \tag{4}$$

In the present work, from the solvolysis of seven bromides (1a-1g) we provided further kinetic evidence to demonstrate the drawback of Hammett-type correlation analysis with respect to the solvent effect. Moreover, the comparison of the correlation analysis of single-term Grunwald-Winstein equation⁹ using Y_{BnBr} (Eqn. 3) and the combination of Y_{Br} and aromatic ring parameter *I* (Eqn. 5)¹⁰ was also studied.

$$\log(k/k_{\circ}) = mY + hI \tag{5}$$

Dedicated to Professor Kung-Tsung Wang on the occasion of his 70th birthday.



RESULTS

1-Aryl-1-tert-butylmethyl bromides 1a-1g were prepared from bromination of the corresponding alcohols (4), which had been synthesized according to Scheme I as was previously described.^{3c} Solvolytic rate constants in various solvents were measured conductimetrically, or titrimetrically for those that had to be monitored at a temperature higher than 85 °C. Reproducible rate constants ($\pm 2\%$) were obtained from duplicate or triplicate runs and were extrapolated by using the Arrhenius equation if they were not measured at 25 °C. Pertinent data at 25 °C are listed in Table 1.

Scheme I



Correlation analyses of log k in Table 1 against σ^* constants¹¹ (Eqn. 3) were carried out, and the results are shown in Table 2. Similar treatment with solvent-dependent σ^* constants ^{2a} yielded the results given in Table 3. The dualparameter Yukawa-Tsuno equation (Eqn. 4) was also employed to analyze the rate data. Table 4 and Table 5 give the results by using σ^* and σ° constants,¹² and by using solventdependent σ^* and σ° constants,^{2a} respectively.

Good linear relationship between log k for 1c against Y_{BnBr}^{6} was observed (Fig. 1). Due to its good solubility in high water-containing binary solvents and reasonable reactivity in many solvents, 1c was chosen to replace 3 as the reference standard for deriving more Y_{BnBr} values. The revised and the extended Y_{BnBr} values are compiled in Table 6. Correlation analyses of log k vs. Y_{BnBr} , and with $Y_{Br}^{13,14}$ and I (Eqn. 5) were carried out for 1a-1g.

DISCUSSION

It is already known that the solvolysis of 1-aryl-1-tertbutylmethyl halides (1 and 2) in ionizing solvents proceeds via limiting S_N1 mechanism.¹⁻³ About one half billion times difference in solvolytic reactivities between the most reactive 1-tert-butyl-1-(4-methoxyphenyl)methyl bromide (1a) to the least reactive 1-tert-butyl-1-(4-trifluoromethylphenyl)methyl bromide (1g) in a variety of solvents could be realized from Table 1. Therefore, it is adequate to carry out Hammett-type correlation analysis for examining the substituent effect on solvolytic reactivity in four different solvents, namely aqueous acetone, aqueous ethanol, aqueous methanol and ethanol-trifluoroethanol mixtures. The results of Brown-Okamoto treatment (Eqn. 1)¹¹ are summarized in Table 2.

Similar to those previously found for 1-aryl-1-tertbutylmethyl chlorides (2),^{3b} excellent linear relationships (correlation coefficient R = 0.994 to 1.00) could be observed in every case. The ρ value is almost constant in different solvents, but varies with the range of substituents under consideration. For instance, it ranges over -6.34 to -6.45 if all seven substrates (1a-1g) are included, and is between -7.38 and -7.50 for parent and activating substrates (1a~1d) only. In addition, ρ values are nearly the same for bromides 1 and chlorides 2, indicating similar resonance contribution of aryl group to the stabilization of the cationic transition state in both systems. The replacement of original σ^{+} constants¹¹ with solvent-dependent σ^* constants^{2a} gave less negative ρ values, which were exhibited in Table 3. It is interesting to note that the variation of ρ values ($\Delta \rho$) with the range of substrates being covered becomes smaller if σ^* (80% ethanol) constants are employed. However, the use of σ^* (80%) acetone) constants resulted in an essentially unchanged $\Delta \rho$ as is already shown in Table 2. Fig. 2 illustrates representative examples of log $k - \sigma^{\dagger}$ correlation analyses. In solvents of both high nucleophilicity, 80E, and low nucleophilicity, 60T40E, significantly upward deviations for data points corresponding to 1f and 1g were realized.

Tables 4 and 5 exhibit the results of Yukawa-Tsuno treatment (Eqn. 2). Excellent linear relationships with ρ values less negative than those observed from Brown-Okamoto treatment (Eqn. 1) could be realized. The ρ and γ values are comparable with those that have been found for the corresponding chlorides,^{3b} which suggest a similar extent of resonance demand¹⁵ at the cationic transition state in the solvolysis of both bromides I and chlorides 2. Comparison of Table 2 and Table 4 indicates the variation of ρ values ($\Delta \rho$) is smaller for single-parameter treatment than dual-parameter treatment when the same number of data points are

	<i>k</i> (s ⁻¹ , 25 °C)							
Solvent ^a	1a	1b	1¢	1d	1e	1f	1g	
100E	3.97×10^{-3}	1.82×10^{-4}	8.26×10^{-7}					
90E	3.56×10^{-2}	1.42×10^{-3}	7.66×10^{-6}					
80E	1.29×10^{-1}	6.22×10^{-3}	3.23×10^{-5}	2.26×10^{-6}	4.18×10^{-7}	1.41×10^{-9}	2.35×10^{-10}	
70E	4.62×10^{-1}	1.88×10^{-2}	1.05×10^{-4}	6.03×10^{-6}	1.33×10^{-6}	4.85×10^{-9}	6.38×10^{-10}	
60E			3.05×10^{-4}		4.59×10^{-6}			
50E			1.23×10^{-3}		1.33×10^{-5}			
40E			5.19×10^{-3}					
90A	1.06×10^{-3}	5.59×10^{-5}						
80A	1.51×10^{-2}	7.31×10^{-4}	4.00×10^{-6}	3.76×10^{-7}	4.02×10^{-8}			
70 A	1.00×10^{-1}	4.38×10^{-3}	2.17×10^{-5}	1.43×10^{-6}	2.87×10^{-7}			
60A	4.57×10^{-1}	2.05×10^{-2}	1.16×10^{-4}	6.48×10^{-6}	1.42×10^{-6}	5.36 x 10 ⁻⁹	7.72×10^{-10}	
50A			5.66×10^{-4}	2.92×10^{-5}	6.50×10^{-6}	2.36×10^{-8}	3.80×10^{-9}	
40A			2.81×10^{-3}					
100 M	7.53×10^{-2}	4.07×10^{-3}	1.80×10^{-5}					
90M	3.38×10^{-1}	1.80×10^{-2}	9.14×10^{-5}	6.02×10^{-6}	8.63×10^{-7}			
80M	1.17	6.73×10^{-2}	3.36×10^{-4}	2.15×10^{-5}	3.22×10^{-6}	1.71×10^{-8}	2.29×10^{-9}	
70M			1.11×10^{-3}					
60M			3.38×10^{-3}	1.85×10^{-4}	3.00×10^{-5}	1.46×10^{-7}	2.57×10^{-8}	
50M			1.08×10^{-2}					
100T			1.36×10^{-2}	1.20×10^{-3}	6.11×10^{-5}	6.32×10^{-7}	1.03×10^{-7}	
80T20E			1.36×10^{-3}	1.06×10^{-4}	9.37×10^{-6}	5.68×10^{-8}		
60T40E	7.69×10^{-1}	5.26×10^{-2}	1.76×10^{-4}	1.66×10^{-5}	1.51×10^{-6}	7.95×10^{-9}	1.25×10^{-9}	
40T60E	1.23×10^{-1}	6.93×10^{-3}	2.68×10^{-5}		2.16×10^{-7}			
97Tw ^b			1.46×10^{-2}		7.00×10^{-5}			
85Tw			1.87×10^{-2}		9.19×10^{-5}			
70 T			2.63×10^{-2}		1.19×10^{-4}			
70 T w			2.92×10^{-2}		1.29×10^{-4}		_	
50T			3.18×10^{-2}	2.38×10^{-3}	1.52×10^{-4}	9.06×10^{-7}	2.42×10^{-7}	
50Tw			3.51×10^{-2}		1.93×10^{-4}			
97Hw			1.07×10^{1c}		2.73×10^{-2}	1.96×10^{-4}		
50H50T			5.38 × 10 ^{1¢}		1.97×10^{-3}	8.80×10^{-6}		

Table 1. Pertinent Rate Constants for Solvolysis of 1-Aryl-1-tert-butylmethyl Bromides

^a For abbreviation of solvents: A = acetone, E = ethanol, M = methanol, T = 2,2,2-trifluoroethanol, H = hexafluoroisopropanol. The numbers denote volume percent of the specific solvent in the mixture, unless mentioned otherwise.

^b A w indicates weight percentage.

^c Extrapolated from $\log k$ (1c) – $\log k$ (1e) and $\log k$ (1c) – $\log k$ (1f) plots.

taken into consideration. For example, the difference between ρ values obtained from 1a to 1e and from 1a to 1g is 0.8~1.0 in Table 2 and is 0.9~1.2 in Table 4. However, no such trend could be found if solvent-dependent substituent constants were used. Moreover, contrary to the general consideration that the variation of the magnitude of γ value is an indication of the significance of resonance contribution,¹⁵ an increasing γ value is found in the case of more deactivating substrates being included.

Similar to those found in Fig. 2, an upward deviation for the data points for strongly deactivating substrates 1f and 1g could also be observed in Fig. 3. Since it happens in solvents of both high nucleophilicity, $80E (N_{OTs} = 0.00^{13})$, and low nucleophilicity, $60T40E (N_{OTs} = -1.01^{13})$, solvent effect other than solvent nucleophilicity should be taken into account. It is likely an additional example of electrophilic acceleration owing to the solvation of leaving group,¹⁶ which would be enhanced especially for substrates containing deactivating substituents. However, in Table 4 the γ values are essentially unchanged for correlation analyses with fixed data points, regardless of the solvent employed. Consequently, the function of solvent is likely to be overshadowed in such a dual-parameter treatment of rate data.

With a few exceptions, the data points in the Grunwald-Winstein plot (Eqn. 1) against Y_{BuBr}^{6} exhibited good linear relationships (Fig. 1). A preliminary study indicated the original Y_{BuBr} values⁶ for some solvents, 100M, 100T, 60A and 50A, might be erroneous, and the value in other bi-

Solvent	Substrate	ρ	R	S.D.ª
80E	1a~1d (n=4)	-7.50	1.00	0.147
	1a~1e (n=5)	-7.18	0.998	0.241
	1a~1f (n=6)	-6.78	0.998	0.232
	1a~1g (n=7)	-6.36	0.995	0.278
70E	1a~1d (n=4)	-7.54	1.00	0.159
	1a~1e (n=5)	-7.22	0.998	0.252
	1a~1f (n= 6)	-6.78	0.997	0.252
	1a~1g (n=7)	-6.40	0.996	0.271
60A	1a~1d (n=4)	-7.49	1.00	0.127
	1a~1e (n=5)	-7.19	0.998	0.232
	1a~1f (n=6)	-6.68	0.997	0.243
	1 a~1g (n=7)	-6.36	0.995	0.274
80M	1a~1d (n=4)	-7.38	0.999	0.170
	1a~1e (n=5)	-7.23	0.999	0.155
	1 a~1f (n=6)	-6.74	0.997	0.245
	1a~1g (n=7)	-6.34	0.995	0.273
60T40E	1a~1d (n=4)	-7.49	0.998	0.324
	1a~1e (n=5)	-7.41	0.999	0.212
	1a~1f (n=6)	-6.90	0.997	0.266
	1a~1g (n=7)	-6.45	0.994	0.305

Table 2. Hammett-Type Correlation Analyses of log k Against σ^* Constants

^a Standard deviation

nary solvents with high water-content was not measurable due to the low solubility of 2-bromo-2-(4-trifluormethyl)adamantane (3).⁷ Since 1-*tert*-butyl-1-(4-methylphenyl)methyl chlorides (2c) has been successfully employed to obtain extended Y_{BoCl} values,³⁴ the corresponding bromide 1c is likely the best choice. Indeed, the good solubility and reasonable reactivity of 1c in many solvents made 1c a better reference standard than 2-bromo-2-(4-trifluormethyl)adamantane (3) for obtaining revised and extended

Table 3. Hammett-Type Correlation Analyses of log k Against Solvent-dependent σ^+ Constants

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Solvent	Parameter	Substrate	ρ	R	S.D. ^a
80E	σ ⁺ (80E)	1a~1d (n=4)	-6.76	0.999	0.180
		1a~1e (n=5)	-6.70	0.999	0.125
		1a~1f (n=6)	-6.53	0.999	0.113
		1a~1g (n=7)	-6.21	0.998	0.194
70E	σ ⁺ (80E)	1a~1d (n=4)	-6.89	1.00	0.108
		1a~1e (n=5)	-6.78	1.00	0.112
		1a~1f (n=6)	-6.54	0.999	0.135
		1a~1g (n=7)	-6.25	0.998	0.187
60 A	σ* (80A)	1a~1d (n=4)	-7.20	0.998	0.314
		1a~1e (n=5)	-7.04	0.998	0.237
		1 a~1f (n=6)	-6.61	0.997	0.241
		1a~1g (n=7)	-6.22	0.995	0.268

^a Standard deviation

 Table 4. Dual-parameter Hammett-Type Correlation Analyses of Log k Against σ° and σ⁺ Constants

Solvent	Substrate	ρ	R	γ
80E	1a~1e (n=5)	-6.43	0.999	1.11
	1a~1f (n=6)	-6.05	0.999	1.17
	1a~1g (n=7)	-5.54	0.999	1.28
70E	1a~1e (n=5)	-6.53	0.998	1.10
	1a-1f (n=6)	-5.95	0.999	1.20
	1a~1g (n=7)	-5.56	0.999	1.28
60A	1a~1e (n=5)	-6.44	0.999	1.11
	1 a~1f (n=6)	-5.92	0.999	1.20
	1a~1g (n=7)	-5.50	0.999	1.29
80M	1a - 1e(n=5)	-6.56	1.00	1.10
	1a~1f (n=6)	-5.83	1.00	1.22
	1a~1g (n=7)	-5.45	0.999	1.31
60T40E	1a~1e (n=5)	-6.72	0.999	1.09
	1a~1f (n=6)	-6.01	0.999	1.21
	1a~1g (n=7)	-5.52	0.999	1.32

Table 5. Dual-parameter Hammett-Type Correlation Analyses of log k Against σ° and Solvent-dependent σ^{*} Constants

Solvent	Parameter	Substrate	ρ	R	γ
80E	σ ⁺ (80E)	1a-1e (n=5)	-6.13	1.00	1.09
		1a~1f (n=6)	-6.12	1.00	1.09
		1a~1g (n=7)	-5.62	0.999	1.19
70E	σ* (80E)	1a-1e (n=5)	-6.22	1.00	1.09
		1a~1f (n=6)	-6.01	1.00	1.12
		1a-1g (n=7)	-5.64	1.00	1.20
60A	σ ⁺ (80A)	1a~1e (n=5)	-5.61	1.00	1.25
		1 a~1f (n=6)	-5.63	1.00	1.24
		1a~1g (n=7)	-5.28	1.00	1.33

Table 6. Compilation of Revised and Extended Y_{BnBr} Values

Solvent ^a	Y _{BaBr}	Solvent ^a	Y _{BuBr}
100E	-1.65 ^b	70M	1.50
90E	-0. 645^b	60 M	1.98
80E	0.00 ^b	50M	2.49
70E	0.457 ^b	100T	2.59
60E	0.940 ^b	70T	2.88
50E	1.54	50T	2.96
40E	2.17 ^b	97Tw	2.63
90A	-2.00 ^b	85Tw	2.73
80A	-0.961 ^b	70Tw	2.92
70 A	-0.204 ^b	50Tw	3.00
60A	0.518	80T20E	1.57 ^b
50A	1.21	60T40E	0.710 ^b
40A	1.90	40T60E	-0.112 ^b
100M	-0.292	97Hw	5.52
90M	-0.393 ^b	50H50T	4.22
80M	0.988 ^b	i-PrOH	-2.55 ^b

^a Abbreviations, same as in Table 1. i-PrOH denotes isopropanol.

^bOriginal values, Ref. 6.

 Y_{BuBr} values (Table 6). Moreover, correlation analysis using the single-parameter Grunwald-Winstein equation (Eqn. 3) produced excellent linear log $k - Y_{BuBr}$ relationships for 1a, 1b, 1d-1g. Table 7 illustrates the results.

Recently, Kevill and coworkers proposed the use of an additional term, aromatic ring parameter I, together with $N_{\rm T}$ and/or Y_x in Eqns. 1 and 2 for studying the solvolytic behavior of benzylic substrates.¹⁰ For limiting S_N1 reactions, the dual-parameter Eqn. 5, instead of the single-parameter Eqn. 1, was used. Among several drawbacks of such an approach,^{17,18} a practical one is the need of a sufficiently large number of experimental data for a reliable analysis. In the series of bromides 1a-1g sufficient data points are available for such a regression. The results are given in Table 8. Obviously, the correlation is less satisfactory in almost every case, and more remarkably, only random order of h and him can be found from the most reactive 1a to the least reactive 1g. In other words, the outcome of the present study could be considered as one more example to demonstrate the superiority of using single-parameter equation (Eqn. 1) with Y_{BnBr} over the dual-parameter equation (Eqn. 5) with Y_{Br} and aromatic ring parameter I in the correlation of solvolytic reactivity for benzylic substrates.

EXPERIMENTAL SECTION

General Remarks

Proton and carbon-13 NMR spectra were recorded on a Bruker Model AC-200 instrument. Infrared spectra were measured on a Perkin-Elmer Model 983G spectrometer.

Table 7. Grunwald-Winstein Type Correlation Analyses of log k Against Y_{BoBr} Value

Substrate	n	m	R	S.D. ^a			
1a	13	1.00	0.998	0.020			
1b	13	1.02	0.997	0.024			
1d	13	0.997	0.997	0.024			
1e	16	0.903	0.993	0.030			
1 f	10	0.963	0.998	0.022			
lg	9	1.03	1.00	0.006			

^a Standard deviation

Elemental analyses were performed in the Microanalytical Laboratory at the Department of Chemistry, National Taiwan University.

Materials

Commercially available spectral-grade or reagentgrade solvents were used directly for preparative purpose. The solvent was purified following conventional methods¹⁹ for kinetic studies. Doubly de-ionized water was used to prepare aqueous solvent mixtures for solvolysis. Bromides 1a to 1g were made from the previously prepared alcohols $(4)^{3c}$ by the reaction with phosphorus tribromide. The overall yields of 1a to 1g from ketones were between 30% to 60% from 50-mmole reactions. Their IR and NMR spectra were found to be in harmony with the assigned structures. The analytical data for new bromides are given as follows: 1-*tert*-Butyl-1-(4-methoxyphenyl)methyl Bromide (1a)

mp. 30-31 °C; Anal. Calcd for C₁₂H₁₇OBr: C, 56.05; H, 6.66%. Found: C, 56.08; H, 6.42%.



Fig. 1. Plots of $\log k$ (1c) against $\log k$ (3).

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Substrate	n	m	R	S.D.ª	h	S.D.*	h/m	
1a	10	0.824	0.980	0.067	1.18	0.233	1.430	
1b	10	0.836	0.985	0.059	1.33	0.206	1.586	
1c	16	0.855	0.992	0.031	0.896	0.138	1.048	
1d	9	0.916	0.993	0.057	0.96	0.173	1.052	
1e	12	0.870	0.989	0.048	0.50	0.157	0.576	
16	7	0.945	0.983	0.094	0 69	0.266	0.726	
1g	6	0.965	0.986	0.100	0.78	0.315	0.812	

Table 8. Correlation Analyses of log k Against YBr and I Values

^a Standard deviation

1-tert-Butyl-1-(4-methylthiophenyl)methyl Bromide (1b)

mp. 73-74 °C; Anal. Calcd for C₁₂H₁₇BrS: C, 52.75; H,

6.27%. Found: C, 52.55; H, 6.18%.

1-tert-Butyl-1-(4-methylphenyl)methyl Bromide (1c)

Anal. Calcd for C₁₂H₁₇Br: C, 59.76; H, 7.10. Found: C, 59.74; H, 7.08%.

1-tert-Butyl-1-(3,5-dimethylthiophenyl)methyl Bromide (1d)

Anal. Calcd for C₁₃H₁₉Br: C, 61.19; H, 7.50%. Found: C, 61.00; H, 7.81%.

1-tert-Butyl-1-(3-chlorophenyl)methyl Bromide (1f)

Anal. Calcd for $C_{11}H_{14}BrCl$: C, 50.51; H, 5.39%. Found: C, 50.49; H, 5.36%.

1-tert-Butyl-1-(4-trifluoromethylphenyl)methyl Bromide (1g)

mp. 90-91 °C; Anal. Calcd for C₁₂H₁₄BrF₃: C, 48.83;

H, 4.78. Found: C, 49.24; H, 4.85%.

Kinetic Measurements

Rate constants were measured at least in duplicate. Conductimetry was employed for solvolyses at 85 °C or at lower temperature. The conductivity cells containing solution of 1×10^{-4} to 1×10^{-5} M were placed in a thermostat with a temperature variation of ± 0.02 °C. A small amount (ca. 0.1%) of 2,6-dimethylpyridine was added to the solution in some cases to prevent curvature of the rate constant plot. The maximum error of k is $\pm 2\%$. The potentiometric titration method was used for those whose rate constants were measured at 90 °C or higher temperatures. The rates of solvolysis were monitored to two to three half-lives in duplicate. Rate constants obtained at other temperatures were extrapolated to those at 25 °C by using Arrhenius plot.



Fig. 2. Correlation analysis using Brown-Okamoto treatment for the solvolysis of 1a~1e (-) and of 1a~1g (-) in 80E (●) and in 60T40E (▲).



Fig. 3. Correlation analysis using Yukawa-Tsuno treatment for the solvolysis of $a\sim1e$ (-) and of $1a\sim1g$ (-) in 80E (● and O) and in 60T40E (▲ and △).

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Key Words

Solvolysis; Hammett-type correlation analysis; Solvent effect; Y_{BnBr} scale.

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