close proximity to the capped biphenyl ring. The magnitude of the upfield shifts of H3 and H5 protons of β-CD upon binding of the guests **1-3** is similar to that caused by ephedrine or pseudoephedrine, suggesting that the substitution at benzylic carbon atom has little effect on the depth of the insertion of the phenyl group into the CD cavity and stability of the inclusion complexes.

References

1. Bender, M. L.; Komiyama, M. *Cyclodextrin Chemistry*; Springer-Verlag: New York, 1978.
2. Li, S.; Purdy, W. C. *Chem. Rev.* **1992**, *92*, 1457 and references cited therein.
3. Wood, D. J.; Hruska, F. E.; Saenger, W. *J. Am. Chem. Soc.* **1977**, *99*, 1735.
4. Rekharsky, M. V.; Goldberg, R. N.; Schwarz, F. P.; Tewari, Y. B.; Ross, P. D.; Yamashoji, Y.; Inoue, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8830.
5. Ikeda, T.; Yoshida, K.; Schneider, H. *J. Am. Chem. Soc.* **1995**, *117*, 1453.
6. Uekama, K.; Imai, T.; Hirayama, F.; Otagiri, M.; Hibi, T.; Yamasaki, M. *Chem. Lett.* **1985**, 61.
7. Dodziuk, H.; Sitkowski, J.; Stefaniak, L.; Jurczak, J.; Sybilska, D. *J. Chem. Soc. Commun.* **1992**, 207.
8. Wenzel, T. J.; Bogyo, M. S.; Lebeau, E. L. *J. Am. Chem. Soc.* **1994**, *116*, 4858, and references therein.
9. Murakami, T.; Harata, K.; Morimoto, S. *Chem. Lett.* **1988**, 553.
10. Uccello-Barretta, G.; Balzano, F.; Caporusso, A. M.; Iodice, A.; Salvadori, P. *J. Org. Chem.* **1995**, *60*, 2227; Uccello-Barretta, G.; Balzano, F.; Menicagli, R.; Salvadori, P. *J. Org. Chem.* **1996**, *61*, 363 and references cited therein.
11. Franza, G.; Mele, A.; Redenti, E.; Ventura, P. *J. Org. Chem.* **1996**, *61*, 909.
12. Tabushi, I.; Shimokawa, K.; Shimidzu, N.; Shirakata, H.; Fujita, K. *J. Am. Chem. Soc.* **1976**, *98*, 7855.
13. Tabushi, I.; Yamamura, K.; Nabeshima, T. *J. Am. Chem. Soc.* **1984**, *106*, 5267.
14. Botsi, A.; Yannakopoulou, K.; Perly, B.; Hadjoudis, E. *J. Org. Chem.* **1995**, *60*, 4017.
15. Hanessian, S.; Benalil, A.; Viet, M. T. P. *Tetrahedron* **1995**, *51*, 10131, and references therein.

Solvent Effects on the Solvolysis of 1-(4-Methoxyphenyl)-1-phenyl-2,2,2-trifluoroethyl Chloride. Influence of an Electron-Withdrawing α-Substituent on Carbonium Ion Center

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Solvolysis rates of 1-(4-methoxyphenyl)-1-phenyl-2,2,2-trifluoroethyl chloride (**1**) and 1-(4-methoxyphenyl)-1-phenylethyl chloride (**2**) were measured in a variety of aqueous binary solvents, and the solvent effect was treated with the Grunwald-Winstein equation. The solvent effect on the solvolysis of **1** failed to give a single linear correlations using the ordinary Y or Y_{Cl}, but exhibited the wide split pattern which could not be related to the solvent nucleophilicity. The improved correlations with Y_{BnCl} and extended dual-parameter treatment, $\log (k/k_o) = mY_{Cl} + hI$ ($m_\Delta Y_\Delta$), were observed for the solvolysis of **1**. These results suggest that the incipient cationic charge in the solvolysis of **1** is delocalized strongly into the aryl-rings in the transition state. While the solvent effect on the solvolysis of **2** is better correlated with Y or Y_{Cl} than Y_{BnCl} but the linearity is not satisfactory. The correlation is comparably improved by the use of the extended Grunwald-Winstein equation, $\log (k/k_o) = 0.81Y_{Cl} + 0.26N_{OTs}$ ($R = 0.994$, $SD = \pm 0.12$), indicating the cationic charge of reaction center of **2** was localized mostly in the transition state.

Introduction

The influence of an electron withdrawing α-substituent in carbonium ion center developed in solvolytic displacement has been studied with important subject.[1] In the previous paper,[2] we have treated the substituent effect on the solvolysis of 1-(4-methoxyphenyl)-1-aryl-2,2,2-trifluoroethyl chlorides based on the Yukawa-Tsuno equation[3] in 80% aqueous ethanol, $\log(k/k_o) = \rho[\sigma^o + r(\sigma^+ - \sigma^o)]$, where r is resonance demand, which is the parameter measuring the degree of resonance interaction between the reaction center and benzene π-system. From the small $|\rho|$ and r values ($\rho = -1.84$ and $r = 0.918$) in comparison with 1-aryl-1-(trifluoromethyl)ethyl tosylates ($\rho = -6.09$ and $r = 1.59$),[4] we concluded that the carbocationic charge in the transition state was dispersed mostly by a strong *p*-π donor, *p*-methoxy group.

Solvent Effects on the tert-Benzylic Chlorides

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Another approach to investigate the mechanism of the solvolysis of α-electron withdrawing substituted benzylic substrate is to apply solvent effect correlation analysis. The Grunwald-Winstein Eq. (1) has been widely utilized as mechanistic probes in the investigation of unimolecular solvolysis reactions.[5] In Eq. (1), k and k_o are the specific rates of solvolyses of a substrate in a given solvent and in 80% ethanol respectively, and m is the sensitivity of the specific rate of solvolysis of a given substrate to the solvent

$$\log\ (k/k_o)=mY+c \qquad (1)$$

ionizing power, Y, which is originally defined by the rate constant in the respective solvent at 25 °C for the solvolysis of *tert*-butyl chloride as a standard S_N1 substrate. For substrates subject to bimolecular attack by the solvent, the decrease of m value is observed with the dispersion between respective binary solvent series, where the dispersal is in proportion to the solvent nucleophilicity, N. Thus the additional lN term was introduced in Eq. (1) for the general description of solvolysis mechanism,[6]

$$\log\ (k/k_o)=mY+lN. \qquad (2)$$

However, the dispersion was observed in the case of the solvent effect of benzylic solvolysis and the splitting for respective binary solvent series was inconsistant with the mechanism of nucleophilic solvent assistance.[7] Schadt, Bentley, and Schleyer pointed out that aryl substrates which yield resonance-stabilized carbonium ions do not give satisfactory correlations with the extended Eq. (2).[8] A wide range of "dispersal" phenomena have been rationalized by differences in solvation between aromatic and aliphatic derivatives.[9] Recently, Liu *et al.* proposed a set of new parameter of ionizing power, Y_{BnCl}, based on solvolysis of 2-chloro-2-(3-chlorophenyl)-adamantane,[10] and demonstrated the good aplicability to some benzylic solvolyses.

In this paper, we have concerned a quantitative explanation of the dispersion pattern of solvent effect on the solvolysis of 1-(4-methoxyphenyl)-1-phenyl-2,2,2-trifluoroethyl chloride (1) and 1-(4-methoxyphenyl)-1-phenylethyl chloride (2). Solvolysis rates of 1 and 2 are measured in a variety of solvent, and solvent effect is analyzed in terms of the Grunwald-Winstein equation.

1   2
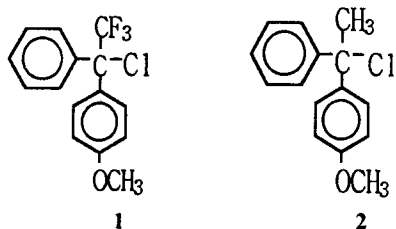
Results and Discussion

Solvolysis rates of 1 and 2 were determined in a variety of solvents. The range of solvents covers aqueous binary mixtures of ethanol, acetone, methanol, and 2,2,2-trifluoroethanol (TFE), and also includes ethanol-TFE mixtures. The rate measurement was carried out by an electroconductimetric method, and the kinetic results are listed in Table 1.

The Y scale based on the solvolysis of *tert*-butyl chloride

Table 1. Rate Constants of the Solvolysis of 1-(4-Methoxyphenyl)-1-phenyl-2,2,2-trifluoroethyl Chloride (1) at 25 °C and 1-(4-Methoxyphenyl)-1-phenyl-ethyl Chloride (2) at 45 °C

Solvent[a]	1	2
	$10^4\ k,\ s^{-1[c]}$	$10^4\ k,\ s^{-1[c]}$
90%EtOH	0.187± 0.001	0.198± 0.001
80%EtOH	0.732± 0.001	0.920± 0.002
70%EtOH	1.99± 0.001	2.84± 0.02
60%EtOH	4.67± 0.01	9.46± 0.03
50%EtOH	9.72± 0.04	26.5± 0.1
40%EtOH	22.6± 0.1	75.5± 0.1
80%Acetone	0.0907± 0.0023	0.0612± 0.0001
70%Acetone	0.413± 0.001	0.604± 0.001
60%Acetone	2.16± 0.01	2.26± 0.01
50%Acetone	6.87± 0.01	9.30± 0.01
40%Acetone	25.3± 0.1	45.2± 0.1
30%Acetone		148± 1
100%MeOH	0.458± 0.001	0.0700[b]± 0.0001
80%MeOH	5.61± 0.01	2.77± 0.01
60%MeOH	22.4± 0.1	28.9± 0.1
50%MeOH	39.7± 0.1	126± 1
100%TFE	207± 1	37.1± 0.1
97%TFE	183± 1	24.1± 0.1
70%TFE	191± 1	82.2± 0.2
50%TFE	74.5± 0.1	
80E-20T	0.254± 0.001	
60E-40T	1.57± 0.01	0.197± 0.001
40E-60T	9.51± 0.01	1.02± 0.01
20E-80T	64.7± 0.3	6.89± 0.01

[a] On a volume-volume basis at 25 °C, except for TFE-H$_2$O mixtures which are on a weight-weight basis. [b] Extrapolated from the data at other temperatures. [c] With a associated standard deviation.

has been shown to contain a component based on the nucleophilic characteristics of the solvent.[11] It has been recommended that this component be eliminated by choosing as the standard substrate 1-adamantyl chloride. Bentley *et al.*[11(a)] defined a Y_{Cl} scale of solvent ionzing power based on the 1-adamantyl chloride. In Figure 1, logarithmic rate constants for the solvolysis of 1 at 25 °C are ploted against the Y_{Cl} values, giving $\log(k/k_o)_1=0.64Y_{Cl}+0.17$ with a fairly poor precision of correlation coefficient ($R=0.928$ and $SD=\pm 0.38$). The solvent parameters used are listed in Table 2.

The mY_{Cl} plot for the solvolysis of 1 did not show a single straight line but exhibited a widely split pattern for binary solvent series as shown in Figure 1. Especially, the plots for less nucleophilic solvets such as aqueous TFE and ethanol-TFE mixtures lie upward from the aqueous ethanol and acetone series. This deviation pattern is not consistent with the pattern anticipated for a mechanistic involvement of the solvent nuceophilicity. In fact, the linearity can not be improved by including the lN term as in Eq. (2), $\log(k/k_o)_1=0.55 Y_{Cl}-0.30N_{OTs}+0.08$ ($R=0.955$, $SD=\pm 0.31$). It is concluded that the solvent effect on the solvolysis of 1 does not give a single linear correlation against either Y or Y_{Cl}, and the split pattern observed in Figure 1 can not be attributed to

Table 2. The Associated Solvent Ionizing Power(Y), Aromatic Ring Parameter(I) and Solvent Nucleophilicity(N) Values

Solvent[a]	Y^b	Y_{Cl}^c	Y_{BnCl}^d	I^e	Y_Δ^f	N_{OTs}^g
100%EtOH	−2.033	−2.500	−1.610	0.20	−0.790	0.00
90%EtOH	−0.747	−0.900	−0.645	−0.281		0.01
80%EtOH	0.000	0.000	0.000	0.00	0.000	0.00
70%EtOH	0.595	0.800	0.571	0.223	−0.05	
60%EtOH	1.124	1.380	1.070	−0.15	0.394	−0.09
50%EtOH	1.655	2.020			0.612	−0.11
40%EtOH	2.196	2.750		−0.24	0.833	−0.22
90%Acetone	−1.856		−2.280	−0.17		
80%Acetone	−0.673	−0.800	−1.090	−0.23	−0.823	−0.42
70%Acetone	0.130	0.170	−0.259	−0.29	−0.454	−0.38
60%Acetone	0.796	1.000	0.518	−0.28	−0.120	−0.34
50%Acetone	1.398	1.730	1.230		0.199	−0.35
40%Acetone	1.981	2.460		−0.35	0.546	−0.39
30%Acetone	2.482	3.210			0.909	−0.40
100%MeOH	−1.090	−1.200	−0.253	0.41	−0.368	−0.04
80%MeOH	0.381	0.670	1.120	0.14	0.298	−0.05
60%MeOH	1.492	2.070		−0.02	0.735	−0.13
50%MeOH	1.972	2.700			0.928	−0.19
100%TFE	1.045	3.030	3.550	0.37	1.277	−3.00
97%TFE	1.148	2.830		0.49	1.123	−2.79
85%TFE	1.347	2.820	3.570		1.092	−1.90
70%TFE	1.659	2.960	3.600	0.25	1.068	−1.20
50%TFE		3.160		0.09		
80E-20T	−1.515	−1.521		0.31	−0.393	−0.19
60E-40T	−0.870	−0.470	0.180	0.43	0.015	−0.55
40E-60T	−0.270	0.711	1.180	0.59	0.428	−1.01
20E-80T	0.406	1.833	2.420	0.52	0.824	−1.72

[a] See footnote a in table 1. [b] $Y = \log(k/k_o)$ for the solvoltsis of *t*-Butyl chloride at 25 ℃, Ref. 5. [c] $Y_{Cl} = \log(k/k_o)$ for the solvolysis of 1-adamantyl chloride at 25 ℃. [d] $Y_{BnCl} = \log(k/k_o)$ for the solvolysis of 2-(3-chlorophenyl)-2-chloroadamantane, Ref. 11. [e] The I value is defined as a $\log(k/k_o) - 1.3Y^+$ (where Y^+ values are are $\log(k/k_o)$ values for 1-adamantyldimetylsulfonium ion solvolysis at 70.4 ℃), Ref. 14. [f] $Y_\Delta = \log(k/k_o)$ for the solvolysis of 4-methoxyneophyl tosylate at 45 ℃, Ref. 13. [g] The N_{OTs} value is defined as a $\log\log(k/k_o)_{MeOTs} - 0.3Y_{OTs}$, Ref. 6.

the nucleophilic solvent assistance. This dispersion phenomena of the plots was observed in solvent effect analyses of solvolyses of other benzylic chlorides, tosylates, and k_Δ substrates,[7,12] and can be reasonably explained by differences in solvent effect between aromatic and aliphatic substrates. The conventional Y_{Cl} parameter based on the solvolysis 1-adamantyl chloride reflects the solvent effect on the solvolyses to form a localized, highly congested carbocation which demands an extensive external stabilization from the solvent. The transition state for a benzylic cation formation, however, is stabilized by π-delocalization of cationic charge into the aryl group, and hence it requires less stabilization by external solvation. This must be the important cause of dispersion of the mY plot.

Thus it is instructive to compare the dispersion behavior with those of other benzylic solvolysis. In Table 3, the corre-
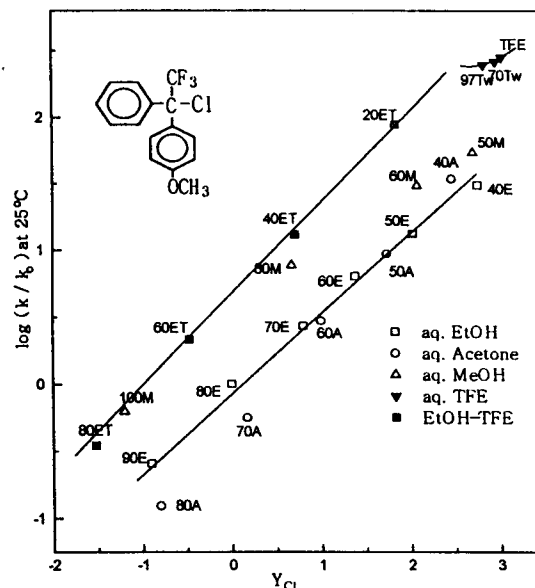
Figure 1. The mY_{Cl} plots for the solvolysis of 1-(4-methoxyphenyl)-1-phenyl-2,2,2-trifluoroethyl chloride at 25 ℃.

Table 3. Correlation Analysis of Solvent Effects on Solvolses of **1** and **2** According to Eq. (1); $\log(k/k_o) = mY_x + c$ and Eq. (2); $\log(k/k_o) = mY_x + lN_{OTs}$

Substrate	Y_x	m	l	c	R^a	n^b
1	Y	0.69±0.14		0.47	0.748	22
		0.61±0.08	−0.64±0.11	0.13	0.923	22
	Y_{Cl}	0.64±0.06		0.17	0.928	22
		0.55±0.05	−0.30±0.09	0.08	0.955	22
	Y_{BnCl}	0.72±0.03		0.02	0.992	15
		0.73±0.04	0.01±0.07	0.03	0.992	15
2	Y	0.96±0.06		0.01	0.961	22
		0.94±0.05	−0.23±0.06	−0.12	0.978	22
	Y_{Cl}	0.74±0.04		−0.23	0.976	22
		0.81±0.02	0.26±0.04	−0.16	0.994	22
	Y_{BnCl}	0.61±0.08		−0.26	0.904	15
		0.81±0.11	0.44±0.18	−0.17	0.937	15

[a] Correlation coefficient. [b] Number of data points involved

lation results for the solvent effect analysis of **1** using Y_{BnCl} based on the solvolysis of 2-chloro-2-(3-chlorophenyl)-adamantane are summarized in comparison with original mY or mY_{Cl} treatments. A distinctly improved linearity with acceptable conformity (R=0.992 and SD=±0.14) indicates the resemblance of the solvent effects in both benzylic solvolysis, $\log(k/k_o) = 0.72Y_{BnCl} + 0.02$.

Rencently, some attempts have been made to determine quantitatively the degree of π-delocalization of the aryl ring. Fujio *et al.* have proposed a new similarity comparison analyis of solvent effects for anchimerically aryl-assisted solvolyses,[13]

$$\log(k/k_{80E}) = m_c Y_{OTs} + m_\Delta Y_\Delta (+ lN_{OTs}). \tag{3}$$

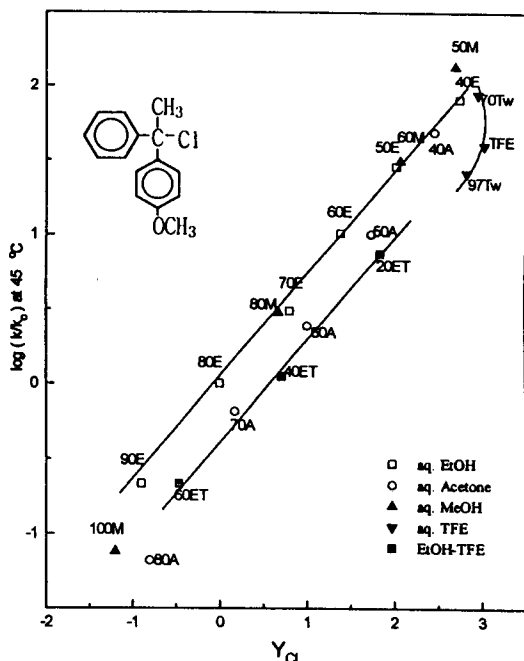In Eq. 3, the Y_{OTs} value of 2-adamantyl tosylate was empolyed

Figure 2. The mY_{Cl} plots for the solvolysis of 1-(4-methoxyphe-nyl)-1-phenyl-ethyl chloride at 45 °C.

as the solvent polarity scale for the extreme of the localized cation and the Y_Δ value of 4-methoxyneophyl tosylate was employed as the solvent polarity scale for the extreme of the delocalized cation. m_c and m_Δ are adjustable blending parameters for the both solvent polarity scales. Also, Kevill *et al.* reported that the introduction of aromatic ring parameter, I, as Eq. (4),[14] showed a considerably improved correlation in the solvent effect of the solvolysis of secondary and tertiary benzylic substrates,

$$\log\ (k/k_o)=mY+hI(+lN_{OTs}).\tag{4}$$

In Eq. (4), I is differences in the nature of the variations of the specific rates of solvolysis of the p-methoxybenzyldi-methylsulfonium ion and of the 1-adamantyldimethylsulfo-nium ion as the solvent composition was altered, and h is the sensitivity toward changes aromatic ring parameter, I,

$$I=\log(k/k_o)_{p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{SMe}_2}-1.3\ \log(k/k_o)_{1-\text{AdSMe}_2}.\tag{5}$$

Solvolyses of **1** were reasonably correlated by Eqs. (3) and (4) as a linear combination of Y_{Cl} and Y_Δ or I as shown in Tables 4 and 5. The samll m and large m_Δ (or h) values indicates that the charge delocalization occurs strongly between the aryl-ring and the carbonium center in the transition state of the solvolysis **1**.

On the other hand, the splitting pattern of the mY plot for the solvolysis of **2** is different from that for **1**. The plots of logarithmic rate constants for the solvolysis of **2** at 45 °C against Y_{Cl} shows also dispersal from linearity as shown in Figure 2,

$$\log(k/k_o)_2=0.74Y_{Cl}-0.23\ \ (\text{R}=0.976,\ \text{SD}=\pm0.23).\tag{6}$$

The plots for aqueous ethanol series lie above those for aqueous acetone series, and aqueous TFE and ethanol-TFE series lie below slightly the aqueous acetone line. This is
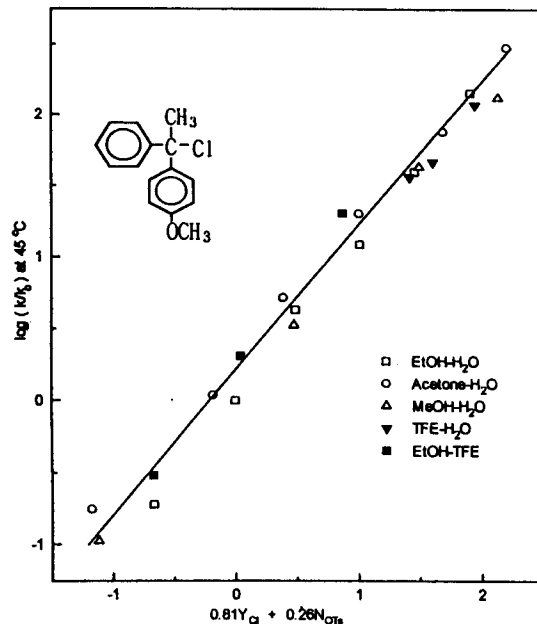

Figure 3. The $mY_{Cl}+lN_{OTs}$ plot for the solvolysis of 1-(4-methox-yphenyl)-1-phenyl-ethyl chloride at 45 °C.

Table 4. Correlation Analysis of Solvent Effects on Solvolses of **1** and **2** According to Eq. (3); $\log\ (k/k_o)=mY_x+m_\Delta Y_\Delta\ (+lN_{OTs})$

Substrate	Y_x	m	m_Δ	l	R^a	n^a
1	Y	0.04 ± 0.07	1.64 ± 0.14		0.974	22
		0.16 ± 0.07	1.28 ± 0.17	-0.22 ± 0.07	0.983	22
	Y_{Cl}	0.17 ± 0.08	1.32 ± 0.20		0.978	22
		0.19 ± 0.07	1.11 ± 0.19	-0.16 ± 0.06	0.985	22
	Y_{BnCl}	0.59 ± 0.10	0.34 ± 0.24		0.993	15
		0.59 ± 0.11	0.34 ± 0.26	0.01 ± 0.07	0.993	15
2	Y	0.67 ± 0.02	0.73 ± 0.05		0.997	22
		0.65 ± 0.03	0.78 ± 0.07	0.03 ± 0.03	0.997	22
	Y_{Cl}	0.75 ± 0.09	-0.03 ± 0.23		0.976	22
		0.68 ± 0.03	0.39 ± 0.09	0.31 ± 0.03	0.997	22
	Y_{BnCl}	0.57 ± 0.33	0.09 ± 0.80		0.904	15
		0.82 ± 0.30	-0.04 ± 0.68	0.44 ± 0.19	0.937	15

^{a} See footnotes a and b of table 3

consistent with the pattern anticipated for a contribution from the solvent nucleophilicity.

In fact, the application of Eq. (2), which adds a term for the solvent nucleophilicity, does effectively improve the correlations ($m=0.81$, $l=0.26$, $R=0.994$, and SD$=\pm0.12$) as shown in Figure 3. However, the the application of Eqs. (3) and (4), which adds a term for Y_Δ and I in the solvent effect of the solvolysis of **2** is showed poor correlation results as shown in Tables 4 and 5. These results indicate that the incipient cationic charge is localized mostly and the nucleo-philic solvent assistance is occurred partly in the transition state of the solvolysis of **2**.

The difference of solvent effect between **1** and **2** is ascri-bable to the different contribution of α-CF$_3$ and α-CH$_3$. The strongly electron-withdrawing CF$_3$ group engendered the un-

Table 5. Correlation Analysis of Solvent Effects on Solvolses of **1** and **2** According to Eq. (5); log $(k/k_o) = mY_x + hI$ $(+lN_{OTs})$

Substrate	Y_x	m	h	l	R^a	n^a
1	Y	0.98 ± 0.05	1.29 ± 0.16		0.985	17
		0.90 ± 0.04	1.88 ± 0.17	-0.19 ± 0.06	0.992	17
	Y_{Cl}	0.66 ± 0.02	1.16 ± 0.10		0.994	17
		0.70 ± 0.03	1.32 ± 0.12	0.10 ± 0.05	0.995	17
2	Y	1.11 ± 0.03	0.96	0.10	0.994	16
		1.09 ± 0.04	0.88 ± 0.14	-0.04 ± 0.05	0.994	16
	Y_{Cl}	0.73 ± 0.04	-0.31 ± 0.17		0.981	16
		0.92 ± 0.03	-0.19 ± 0.11	0.31 ± 0.05	0.996	16

^{a} See footnotes a and b of table 3
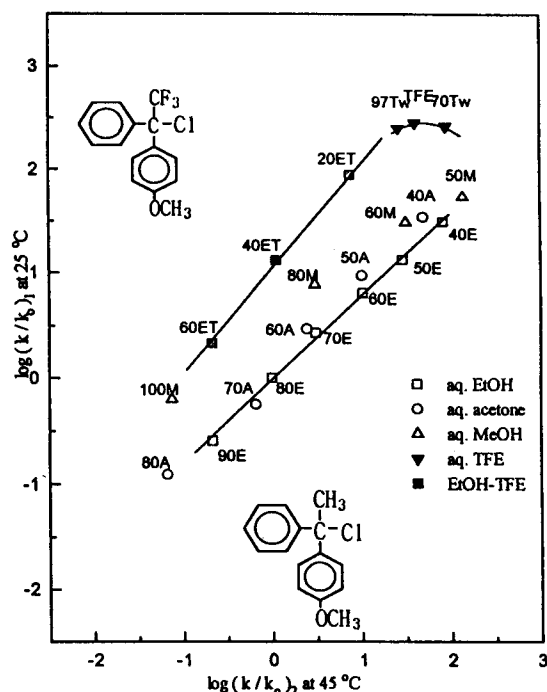
Figure 4. Linear logarithmic rate relation for solvolyses of 1-(4-methoxyphenyl)-1-phenylethyl chloride at 45 ℃ against 1-(4-methoxyphenyl)-1-phenyl-2,2,2-trifluoroethyl chloride at 25 ℃.

stable carbocartionic center, which is needed high electron demand for stabilization by electron donation from the aryl group. The difference in the splitting behavior can be shown by the direct comparison between closely smillar solvolysis. In Figure 4, logarithmic solvolysis rates of **1** are plotted against those for **2**,

$$\log(k/k_o)_2 = 0.83 \ \log(k/k_o)_1 + 0.37 \quad (R = 0.869, \ SD = \pm 0.50). \quad (7)$$

The splitting pattern of Figure 4 exhibits simillar to that of Figure 1; less nucleophilic fluorinated alcohol mixtures show upward deviation from high nucleophilic solvents such as aqueous alcohol and acetone series. As already pointed out, the deviation behavior observed in Figure 4 can not be accounted for by the nucleophilic solvent assistance but be interpreted as the result of delocalization of the developing cationic charge in the transition state.

The inclusion of hI term to Eq. (7) considerably improves

the correlation,

$$\log(k/k_o)_1 = 0.90 \ \log(k/k_o)_2 + 1.43I + 0.30$$
$$(R = 0.988, \ SD = \pm 0.17, \ n = 16). \quad (8)$$

It is quite evident from Figure 4 and Eq. (8) that the charge delocalization in the transition state of the solvolysis of **1** is larger than that of **2**.

In conclusion, the dispersion behavior of the solvent effect in the solvolysis of α-CF_3 system, **1**, must arise from a direct involvement of the aryl π-system in the delocalization of the carbocationic charge in the transition state, while the carbocationic center of α-CH_3 system, **2**, is not delocalized. We will extended the mechanistic investigation of the solvent effects on the wide range of substituents of 1-(4-methoxyphenyl)-1-aryl-2,2,2-trifluoroethyl chlorides.

Experimental

General remarks. ^1H NMR spectra were recorded on a Bruker AM-300 Spectrometer with TMS as an internal standard. Mass spectral analysis was obtained with HP 5890 series II GC/5970 instrument. For the isolation and identification of synthetic materials were used sillica gel and Art 5554 DC-Alufolien Kieselgel 60 F_{254} from Merk.

Materials. Organic solvents and water for the kinetic studies were purified as described earlier.[15] The binary mixtures were prepared by mixing the corresponding volumes or weights of the pure solvent at 25 ℃. 1-(4-Methoxyphenyl)-1-phenyl-2,2,2-trifluoroethyl chloride was prepared from 1-(4-methoxyphenyl)-1-phenyl-2,2,2-trifluoroethanol and thionyl chloride, as described previously,[2] oil; ^1H NMR ($CDCl_3$) δ 3.81 (s, 3H, OCH_3), 6.84-7.52 (m, 9H, Ar). 1-(4-Methoxyphenyl)-1-phenylethyl chloride was prepared from 1-(4-methoxyphenyl)-1-phenylethanol and thionyl chloride, oil; ^1H NMR ($CDCl_3$) δ 2.21 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 6.80-7.41 (m, 9H, Ar).

Kinetic Measurement. Solvolysis rates were measured by an electroconductimetric method.[14(a)] Conductance measurements were made in a cell with platinium electrodes using approximately a 25 cm^3 solution at an initial concentration of 10^{-4} mol/L of substrate. 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 at least 80 points for three half-lives and an infinity reading was taken after 10 half-lives. The first-order rate constants were determined by least squres computer program and gave excellent first-order behavior with correlation coefficient of greater than 0.9999.

References

1. (a) Gassman, P. G.; Talley, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 1214. (b) Koshy, K. M.; Tidwell, T. T. *J. Am. Chem. Soc.* **1980**, *102*, 1216. (c) Liu, K. T.; Sheu, C. F. *Tetrahed-*

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Bull. Korean Chem. Soc. **1996**, Vol. 17, No. 11 1061

ron Letters **1980**, *21*, 4091.

2. Yoh, S.-D.; Kweon, J. M.; Byeon, S. I.; Fujio, M.; Mishima. M.; Tsuno, Y. *Bull. Korean Chem. Soc.* **1996**, *17*(3), 228.

3. (a) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 971. (b) Yukawa, Y.; Tsuno, Y.; Sawada, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2274.

4. Liu, K. T.; Kuo, M. Y.; Sheu, C. F. *J. Am. Chem. Soc.* **1982**, *104*, 211.

5. Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.

6. Winstein, S.; Grunwald, E.; Jones, H. W. *J. Am. Chem. Soc.* **1951**, *73*, 2770.

7. (a) Fujio, M.; Goto, M.; Funatsu, K.; Yoshino, T.; Tsuno, Y. *Mem. Fac. Sci. Kyushu Univ. Ser. C,* **1990**, *17*(2), 255. (b) Fujio, M.; Goto, M.; Funatsu, K.; Yoshino, T.; Saeki, Y.; Yatsugi, K.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 46. (c) Kevil, D. N.; Ismail, N. HJ.; D'Souza, M. J. *J. Org. Chem.* **1994**, *59*, 6303. (d) Bently, T. W.; Koo, I. S.; Norman, S. J. *J. Org. Chem.* **1991**, *56*, 1604.

8. (a) Schadt, F. L.; Bently, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667. (b) Bently, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1. (c) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1991**, *56*, 1845.

9. (a) Dau-Schmidt, J. P.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1991**, *17*, 121. (b) Fainberg, A. H.; Winstein, S.

J. Am. Chem. Soc. **1957**, *79*, 1597, 1602. (c) Fujio, M.; Tomita, N.; Tsuno, Y.; Kobayashi, S.; Taniguchi, H.; Kaspi. J.; Rappoport, Z. *Tetrahedron Lett.* **1992**, *33*, 1309. (d) Bently, T. W.; Dau-Schmidt, J. P.; Llewellyn, G.; Mayr, H. *J. Org. Chem.* **1992**, *57*, 1791.

10. Liu, K. T.; Sheu, H. C. *J. Org. Chem.* **1991**, *56*, 3021.

11. (a) Bently, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5471. (b) Bently, T. W.; Roberts, K. *J. Chem. Soc., Perkin Trans. 2.* **1989**, 1055.

12. Fujio, M.; Susuki, T.; Goto, N.; Tsuji, Y.; Yatsugi, K.; Saeki, Y.; Kim, S. H.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2233.

13. (a) Fujio, M.; Saeki, Y.; Nakamoto, K.; Yatsugi, K.; Goto, N.; Kim, S. H.; Tsuji, Y.; Rappoport, Z.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2603. (b) Fujio, M.; Susuki, T.; Yatsugi, K.; Saeki, Y.; Goto, N.; Kim, S. H.; Tsuji, Y.; Rappoport, Z.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2619.

14. (a) Kevil, D. N.; Aderson, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 1579. (b) Kevil, D. N.; D'Souza, M. J. *J. Chem. Soc., Perkin. Trans. 2.* **1995**, 973. (c) Kevil, D. N.; Bahnke. *J. Chem. Soc., Perkin. Trans. 2.* **1995**, 1777.

15. Perrin, D. N.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon press: New York, 1988.

Tetrathiafulvalene (TTF) Charge Transfer Compounds with Some Heavier Transition Metal (Au, Pt, Ir, Os) Chlorides

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The charge transfer compounds of tetrathiafulvalene (TTF) with the general formula of $(TTF)_mMCl_n$ (M=Au, Pt, Ir, Os) were prepared by the direct reaction using excess $HAuCl_4 \cdot 3H_2O$, $H_2PtCl_6 \cdot xH_2O$, $H_2IrCl_6 \cdot xH_2O$ and H_2OsCl_6 respectively. The powdered electrical conductivities (σ_{rt}) at room temperature are given as follows; $(TTF)_3AuCl_2$, 4.53×10^{-3}; $(TTF)_{3.5}AuCl_2$, 6.37×10^{-3}; $(TTF)_3PtCl_4$, 5.51×10^{-4}; $(TTF)_2IrCl_4$, 2.40×10^{-5}; $(TTF)OsCl_4 \cdot 1/2C_2H_5OH$, 4.46×10^{-7} Scm^{-1}. Magnetic susceptibility, electronic (UV-Vis.), vibrational (IR) and EPR spectroscopic evidences indicate that there is incomplete charge transfer from the TTF donor to gold, platinum, and iridium respectively, and that there is essentially complete charge transfer to osmium, thereby resulting a relatively low electrical conductivity in osmium compound. The EPR and magnetic susceptibility data reflect that the metals are in diamagnetic Au(I), Pt(II), Ir(III), and Os(II) oxidation states, and the odd electrons are extensively delocalized over the TTF lattices in each compound.

Introduction

Tetrathiafulvalene (TTF) has been used as an electron donor to form highly conductive charge transfer compounds. The structural and electronic properties of TTF are considered to be important determinants of electrical-transport properties in crystals of conductive materials. The most famous

compound, TTF-TCNQ (TCNQ=tetracyanoquinodimethane) exhibits highly metallic conductivity which rises to almost 10^4 Scm^{-1} at around 55 K.[1~3] It has been concluded that compounds with high electrical conductivities should be formed from donor-acceptor molecules that are in partial oxidation states with uniform structures containing segregated stacks of the constituent molecules.[1,4] We have prepared[5,6]