

wherein R^1 , R^2 , R^3 may independantly be Cl or methyl.

As shown in Table 3, trisilaalkanes, Formular II, were obtained in much higher yields compared with the literature values. The highest selectivity for trisilaalkanes was obtained from the reaction of α -chloromethyltrimethylsilane, 7, and the lowest from α -chloromethyltrichlorosilane, 18. Higher amount of by-products were obtained from the reaction of highly chlorinated silanes, while smaller amount of by-products from highly methylated silanes.

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Contribution of Electrophilic Interference on Solvolytic Reactions in Fluorinated Alcohol Mixtures

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The degree of electrophilic interference on the solvolytic reactions of model substrates has been studied in fluorinated alcohol solvent mixtures. With variation of solvent composition of 1,1,1,3,3,3-hexafluoro-2-propanol(HFP) and 2-propanol (PrOH) mixtures, the magnitude of electrophilic solvent assistance was changed inversely with the degree of nucleophilic solvent assistance. The contribution of electrophilic interference for 2-adamantyl tosylate showed higher than *tert*-butyl chloride in HFP-PrOH mixtures. Through a correlation of nucleophilic solvent assistance and electrophilic solvent assistance based on the method of double differences, HFP-PrOH mixture showed a big discrepancy from non-fluorinated alcohol systems.

Introduction

Solvent nucleophilicity has been of considerable interest in the study of solvent effect¹. In particular, weak nucleophilic media such as carboxylic acids or fluorinated alcohols are well recognized to show a very different solvent effect comparing with the hydroxylic solvents such as water and alcohols in various solvent-assisted reactions.^{1b} Carboxylic acids and fluorinated alcohols show a weak nucleophilic property in the solvolytic reactions of the model substrate of

tert-butyl chloride² and 2-adamantyl tosylate³. Fluorinated alcohols which are substituted fluorine instead of hydrogen should exhibit a very weak acidity⁴. Weak acidity of fluorinated alcohols are considerably sensitive to the nucleophilic solvent-assisted reactions.

Solvent properties were investigated widely for trifluoroethanol(TFE)⁵ and 1,1,1,3,3,3-hexafluoro-2-propanol(HFP)⁶ in order to determine their nucleophilicity(N) and ionizing power(Y) in many fluorinated alcohols. TFE and HFP are shown different solvent effect by nucleophilic solvent assist-

Table 1. Pseudo First-Order Constants for Solvolyses of *tert*-Butyl Halides and 2-Adamantyl Tosylate in 1,1,1,3,3,3-Hexafluoro-2-Propanol and 2-Propanol Mixtures at Various Temperatures

Substrates	Temp. (°C)	$k_1 \times 10^5$ (sec ⁻¹)								
		2-PrOH (v/v%) Content	10	20	30	35	40	50	70	
<i>tert</i> -BuCl	25		174	52.9	11.0	4.64	1.70	0.446	0.0306	
	30		322	93.3	20.2	8.67	3.04	0.829	0.0641	
	35		551	170	35.4	15.2	5.75	1.51	0.122	
<i>tert</i> -BuBr	25		—	199	91.5	43.1	26.7	10.8	0.907	
	30		—	330	160	80.2	54.8	15.9	1.67	
	35		—	520	269	136	93.2	29.6	2.90	
<i>tert</i> -BuI	25		—	380	124	103	64.9	11.9	3.26	
	30		—	563	187	159	106	25.0	7.06	
	35		—	815	284	252	170	50.5	13.9	
2-AdOTs		2-PrOH(v/v%) Content								
			5	10	15	20	25	30	50	70
	48		131	75.7	50.3	23.4	12.5	5.61	1.98	0.128
	50		153	91.0	61.2	29.3	15.9	7.12	2.59	0.168
	52		172	114	77.9	37.3	20.1	9.15	3.27	0.226

ance(NSA)⁷ in the solvolyses of model substrates, *tert*-butyl chloride and 2-adamantyl chloride⁸.

Even though several methods^{9,10} were applied for estimating of the extent of NSA there are still remained problems such as an anomaly for correlation of solvent effect in fluorinated alcohol and their solvent mixtures.

In the solvolytic reactions using a model substrate, an electrophilic solvent role might be contributed so much to the solvolytic reactions of model substrates. Especially the electrophilic solvent assistance(ESA) would be observed highly with variation of solvent compositions HFP and 2-propanol (PrOH) binary mixtures. If NSA and ESA for the wide range of solvent composition of HFP-PrOH solvent mixtures are applied simultaneously to the solvolyses of 2-adamantyl tosylate and *tert*-butyl halides, it would be satisfied to solve the contradiction in terms of the anomaly shown in by previous studies⁸⁻¹⁰.

On the above consideration we have investigated to use the method of estimating nucleophilic assistance including electrophilic assistance in various content of HFP-PrOH mixtures. In order to determine the contribution of electrophilic interference using the ionizing power based on model substrates for the limiting S_N1 mechanism *tert*-butyl halides and 2-adamantyl tosylate, the solvolytic reactions of *tert*-butyl halides and 2-adamantyl tosylate are studied in HFP-PrOH mixtures by a conductometrical kinetic method.

Experimental

Material. HFP was commercial (Aldrich, 99+ %) product and was used the anhydrous HFP after stored over silica gel beads. 2-Adamantyl tosylate(2-AdOTs) was prepared from 2-adamantanol and tosyl chloride in pyridine at 0°C and was purified by crystallization from hexane, m.p. 83-84°C ¹H-NMR (CDCl₃): δ 1.27-2.30(m, 14 adamantyl), δ 2.4(s, 3H), δ 4.60(s, 1H), δ 7.26(d, 2H, J=8Hz), δ 7.75(d, 2H, J=8Hz). PrOH was commercial(Aldrich, 99+ %) product packaged under nitrogen and was used the anhydrous PrOH after stored over molecu-

lar sieves. *tert*-Butyl chloride(*tert*-BuCl), *tert*-butyl bromide (*tert*-BuBr) and *tert*-butyl iodide(*tert*-BuI) were commercial samples, which were used after purified as described previously¹¹. Solvent mixtures were prepared in volume percentages(v/v%).

Kinetic Method. The rates were followed conductrimetrically¹¹ and the k_{obs} values were obtained by the Guggenheim method¹². The values listed in Table 1 are the averages of several runs with a reproducibility of $>\pm 3\%$ in all cases.

Results and Discussion

The reactivities of *tert*-butyl halides(*tert*-BuX) and 2-AdOTs in HFP-PrOH binary solvent mixtures are shown as the order of magnitude, *tert*-BuI > *tert*-BuBr > *tert*-BuCl > 2-AdOTs, which is inversely proportional to the intensity of bonding as reported previously¹¹ as in the isodielectric binary solvent mixtures, as shown in Table 1. This is in accord with a typical illustration of S_N1 ¹³ that the rate determining step corresponds to the slow bond breaking step of C-X bond to form the carbocation. The rate to produce carbocation accelerates rapidly with changing from the good leaving group to the poor leaving group in Table 1.

Comparing with the rate constants of each substrate in Table 1, the rate constants of *tert*-BuX are shown to be much higher than the ones of 2-AdOTs. It is implicated with the solvolytic reaction mechanism of 2-AdOTs might not be involved with S_N2 mechanism. *tert*-BuCl has been used widely for a long time to find the limiting S_N1 mechanism because the compound has been known to be involved the rate-limiting formation of carbocation or ion pair without nucleophilic solvent assistance¹⁴. Recently, however this suggestion was criticized because there is an evidence¹⁴ that solvolysis of *tert*-BuCl is involved partial formation of a covalent bond at the rearside. There is a possibility for a whole range of extents to which the nucleophile can assist heterolytic cleavage. There is a wide difference between *tert*-BuX and 2-AdOTs in a view of the substrate effect to compare with

Table 2. Activation Parameters, ΔH^\ddagger (Kcal \cdot mol $^{-1}$), $-\Delta S^\ddagger$ (e.u.), for Solvolyses of *tert*-Butyl Halides and 2-Adamantyl Tosylate in 1,1,1,3,3,3-Hexafluoro-2-Propanol and 2-Propanol Mixtures

Solvent Mixtures (v/v%)	<i>t</i> -BuCl		<i>t</i> -BuBr		<i>t</i> -BuI		2-AdOTs	
	ΔH^\ddagger	$-\Delta S^\ddagger$	ΔH^\ddagger	$-\Delta S^\ddagger$	ΔH^\ddagger	$-\Delta S^\ddagger$	ΔH^\ddagger	$-\Delta S^\ddagger$
5 PrOH	—	—	—	—	—	—	15.8	18.7
10 PrOH	20.4	2.70	—	—	—	—	20.5	4.02
15 PrOH	—	—	—	—	—	—	22.1	-0.54
20 PrOH	20.7	4.10	13.3	14.2	16.9	25.0	23.6	-4.05
25 PrOH	—	—	—	—	—	—	24.1	-4.48
30 PrOH	20.8	6.85	14.5	8.34	19.1	23.2	24.8	-5.24
35 PrOH	21.0	8.56	15.8	5.81	20.3	19.2	—	—
40 PrOH	21.6	7.86	17.0	0.380	22.2	16.1	—	—
50 PrOH	22.6	7.17	17.8	-10.1	25.8	16.9	25.5	-5.52
70 PrOH	24.7	5.45	20.6	-7.86	25.9	12.5	29.0	-11.8

rate constants in Table 1.

Though *tert*-BuCl and 2-AdOTs are model substrates in the S_N1 -limiting solvolysis, the rate constants of *tert*-BuCl are shown higher than those of 2-AdOTs.

This seems that it is not excluded the mechanistic change-over by S_N2 reaction conditions. Therefore the nucleophilic solvent participation in 2-AdOTs solvolysis is apparent to be well prevented more than *tert*-BuX solvolyses. A penta-coordinate intermediate or transition state in 2-AdOTs solvolysis should be strongly hindered by axial hydrogen atoms of adamantane cage molecule. This is supported by showing the low reactivity of 2-AdOTs even under an influence of solvent such as strong S_N2 reaction conditions⁹.

The rate constants in Table 1 vary widely as the solvent composition varies. These results show a variation of 6×10^1 - 5×10^3 in the relative rates of solvolyses of *tert*-BuX and 2-AdOTs as increasing the content of HFP.

Comparing with two substrate systems in binary solvent mixtures, the relative rates for *tert*-BuX and 2-AdOTs change from 1.0×10^3 to 5.7×10^3 as variation of binary solvent composition from 5% (v/v) or 10% (v/v) to 70% (v/v).

This phenomenon is presumably caused by a weak acidity of HFP. Various different physical properties reveal the pK_a value of HFP in water: for HFP, $pK_a=9.30$, which is about 7 pK_a units more acidic than that of *op* PrOH¹⁵ because pK_a of 2-PrOH is 16.3.

The acidic property of HFP arises presumably because of strong electron withdrawal by the two CF_3 groups¹⁶. This electronic effect also reduces the nucleophilicity or cation-solvating power of HFP, and the reduced availability of the oxygen lone pair is reflected in the high first ionization energy of HFP as reported previously as 12.35 eV¹⁷. This value is higher than the first ionization energy of TFE, 11.75 eV and also higher than that of EtOH, 10.46 eV.

The rate data cited Table 1 support the tendency of the first ionizing energy illustrates the evidence that HFP has less nucleophilic property than PrOH.

Activation parameters, ΔH^\ddagger and ΔS^\ddagger , for the solvolyses of *tert*-BuX and 2-AdOTs in HFP-PrOH binary solvent mixtures are shown in Table 2.

The results in Table 2 illustrate that the solvolytic reaction mechanisms of *tert*-BuCl and 2-AdOTs get closer to the S_N1

Table 3. Various Ionizing Power (Y_X)^c Scale for 1,1,1,3,3,3-Hexafluoro-2-Propanol and 2-Propanol Mixtures at 25°C

Solvent (v/v%)	Y_{t-BuCl}^d	Y_{t-BuBr}^e	Y_{t-BuI}^f	$Y_{2-AdOTs}^g$
5 PrOH	—	—	—	3.94
10 PrOH	2.29	—	—	3.74
15 PrOH	—	—	—	3.73
20 PrOH	1.77	1.03	0.315	3.60
25 PrOH	—	—	—	3.27
30 PrOH	0.994	0.459	0.0194	2.56
35 PrOH	0.726	0.258	-0.323	—
40 PrOH	0.373	-0.241	-0.416	—
50 PrOH	-0.329	-0.523	-0.887	1.97
70 PrOH	-1.50	-1.70	-1.46	-0.236

^a $Y_X = \log[k(\text{studied solvent})/k_0(80\% \text{ EtOH-H}_2\text{O})]$. ^b The data were calculated from the original rate constant, $k_0(80\% \text{ EtOH-H}_2\text{O})=9.24 \times 10^{-6} \text{ s}^{-1}$ at 25°C (E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948)). ^c The data were calculated from the original rate constant, $k_0(80\% \text{ EtOH-H}_2\text{O})=3.58 \times 10^{-4} \text{ s}^{-1}$ at 25°C (A.H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956)). ^d The data were calculated from the original rate constant, $k_0(80\% \text{ EtOH-H}_2\text{O})=9.26 \times 10^{-4} \text{ s}^{-1}$ at 25°C (J. Shorter and C. Hinselwood, *J. Chem. Soc.*, 2412 (1949)). ^e The data were calculated from the original rate constant, $k_0(80\% \text{ EtOH-H}_2\text{O})=2.30 \times 10^{-8} \text{ s}^{-1}$ at 25°C (D. N. Kevill and D. C. Hawkinson, *J. Org. Chem.*, **54**, 154 (1989) here OTs means 2-AdOTs).

character based on the criterion of the generalization by Pritt and Whiting's proposal¹⁸ as shown the ΔH^\ddagger values of *tert*-BuCl and 2-AdOTs are higher than 20 Kcal \cdot mol $^{-1}$, while ΔS^\ddagger values are very low with a few exception compared to *tert*-BuBr and the activation parameters for *tert*-BuI illustrate the dubious basis of the generalization of S_N1 criterion by activation parameters.

The various Y_X scales of solvent ionizing power based on the Grunwald-Winstein(GW) equation¹⁹ and T_{OTs} scales of solvent ionizing power suggested by Bentley, Schadt and Schleyer^{20,21} are summarized in Table 3.

Here Y_X scales were calculated from the original GW Eq.,

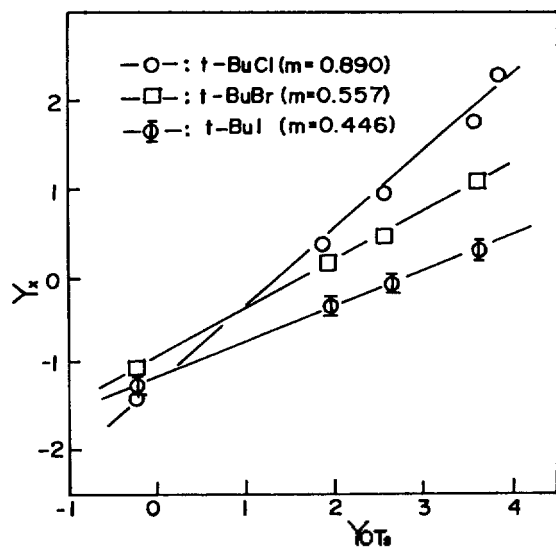


Figure 1. Correlation of Y_X versus Y_{OTs} .

that is, the rate constant, k is for the solvolytic reaction of *tert*-butyl chloride in the solvent system of HFP-PrOH being studied, and k_0 is the solvolytic rate constant of *tert*-butyl chloride in 80% ethanol-water at 25°C as defined the solvent ionizing power Y_X as following (1):

$$\log (k/k_0)_{tert-BuCl} = Y_X \quad (1)$$

Y_{OTs} scales were determined by the modified GW Eq. suggested by Bentley *et al.*

$$\log (k/k_0)_{2-AdOTs} = Y_{OTs} \quad (2)$$

In Eq. (2), k is the solvolytic rate constant for the solvolytic reaction of 2-adamantyl tosylate in the solvent system of HFP-PrOH mixture and k_0 is the solvolytic rate constant of 2-adamantyl tosylate in 80% ethanol-water mixtures.

Y_{Br} and Y_I values are provided substantially lower than corresponding Y_{OTs} values for HFP-PrOH mixtures because of the high reactivities of *tert*-BuBr and *tert*-BuI. These anomalous behaviour of *tert*-BuBr and *tert*-BuI may be associated with the weakly basic nature of the leaving groups, thus the trends are explained by electrostatic effects due to charge delocalization on anions of different sizes²². This anionic effect by electrostatic trends may reveal apparently on the slopes m which is included the correlation of GW equation,

$$\log (k/k_0) = m Y \quad (3)$$

To find a useful information from the correlation, the trends of m for Y_X and Y_{OTs} are shown in Figure 1.

The slopes show for Y_{Cl} , $m=0.890$, for Y_{Br} , $m=0.557$ and for Y_I , $m=0.446$ in Figure 1. m values of Y_{Br} and Y_I give significantly smaller than 1.00 probably because the delocalization of positive charge contributes in the transition state by neighbouring group participation of the solvent molecules. The electrostatic effects due to charge delocalization are shown to vary steeply according to change from Y_{Cl} to Y_I . This trends are explicable that Y_{Cl} can be reflected to be almost the limiting S_N1 mechanism similar to the one in HFP-PrOH binary mixtures.

Even if 2-AdOTs and *tert*-BuCl are good model substrates, their solvolytic rate constants show a dependence upon varia-

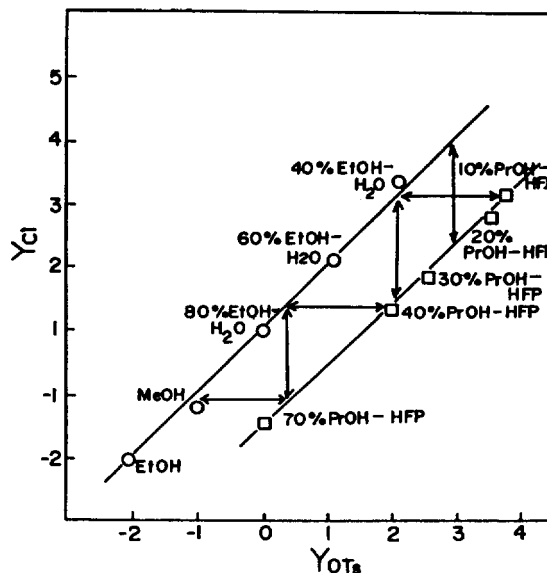


Figure 2. Correlation of Y_X values of solvolysis rates for 2-adamantyl tosylate versus *tert*-butyl chlorides at 25°C.

tion of solvent composition as shown in Table 1. This dependence on solvent composition is presumably attributed to a property of electrophilic solvent assistance (ESA) for HFP-PrOH solvent mixtures.

ESA is well known to participate as a neighbouring group in solvolytic reactions²³. Schleyer *et al.*²³ has indicated that solvolyses of 2-adamantyl substrate has brought up a problem from their earlier studies²⁴ that the reaction proceeds competitively between nucleophilically solvent assisted and anchimerically solvent assisted processes. They defined this anchimerically assisted process as an electrophilic solvent assistance (ESA). Harris *et al.*³, who have reported that the degree of ESA means a measure of the electrophilic interference. The electrophilic interference in the solvolytic reaction can be determined by the method of double difference (MODD) which has been proposed by Harris *et al.*³.

Figure 2 shows that a correlation of NSA and ESA in the solvolyses of two model substrates, *tert*-BuCl and 2-AdOTs in various compositions of HFP-PrOH binary solvent mixtures based on MODD.

The line of HFP-PrOH mixture is not overlapped with the line of non-fluorinated protic solvent systems as shown in Figure 2. This is caused by a deviation from a typical tendency of nucleophilically solvent assisted substrate reacting with NAS solvent²⁵.

A difference of \log unit according to vertical axis between the upper line and lower shows 1.5 and the one according to horizontal axis between the two lines indicates 1.8 in Figure 2.

The contribution to NSA for *tert*-BuCl solvolysis has reported to be 0.4 \log unit²⁶ with variation of solvent composition. From the two lines ESA contribution can be calculated so that the remaining 1.1 \log unit results from enhanced sensitivity to electrophilicity on the part of 2-AdOTs.

From the results which are calculated for ESA to affect to 2-AdOTs substrate, the electrophilic interference can be compared with the difference to be showed by MODD in rates between the two lines. Thus, ESA must account for

1.4 log unit.

These works show that 1.1 log unit and 1.4 log unit are very higher values compared to those⁹ of ethanol (EtOH)-trifluoroethanol (TFE) mixtures. It means that HFP-PrOH mixtures give a large contribution of ESA to the two model substrates compared to EtOH-TFE mixtures. The contribution of electrophilic interference for 2-AdOTs shows also higher than *tert*-BuCl in HFP-PrOH mixtures and this effect reveals clearly in proportion to from high nucleophilic solvent to lower nucleophilic solvent systems such as HFP.

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