Solvolysis of 2-Aryl-2-chloro-4,4-dimethylpentanes. Confirmation of Validity of Brown−Okamoto σ^+ Constants

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Specific rate constants of solvolysis in 90% aqueous acetone have been determined at 25 °C for 10 2-aryl-2-chloro-4,4-dimethylpentanes (**3**) having a substituent *p*-cycPr, *p*-Me, *m*-Me, *p*-F, (H), *p*-Cl, *m*-Cl, *m*-CF_3, *p*-CF_3, or *p*-NO_2. The Hammett−Brown relation is satisfactorily linear ($r = 0.999$) with ρ^+ of −4.51, showing that Brown−Okamoto σ^+ values based on the solvolysis of the cumyl chloride system **1** are widely usable for the substrates solvolyzing without appreciable nucleophilic solvent participation. Solvolysis of **3** having 3,5-Cl_2 or 3,5-$(CF_3)_2$ substituents suggests the use of σ^+ values of +0.740 and +0.982 instead of respective $2\sigma_m{}^+$ values of +0.798 and +1.040. The large negative ρ^+ values in TFE of −5.91 and −5.63 for **1** and **3**, respectively, reflect decreased nucleophilic (or Brønsted base type) solvation. Comparison of solvolysis rates of **1** with **3**, both having *m*-Cl, *p*-CF_3, or 3,5-$(CF_3)_2$ substituents, in aqueous ethanol, aqueous acetone, TFE, and TFE−EtOH suggests that nucleophilic intervention by solvent in the cumyl system increases as the intermediate carbocation becomes more electron-demanding.

Introduction

One of the most important structure−reactivity relationships in organic chemistry is the Hammett equation (eq 1), where k (or K) and k_0 (or K_0) are the specific rate (or equilibrium) constants of a given compound having a substituent and of an unsubstituted one, respectively, σ is a substituent constant that is defined by eq 2, (where K and K_0 are dissociation constants of substituted and unsubstituted benzoic acids, respectively, in water at 25 °C) and ρ is a reaction constant.

$$\log(k/k_0) = \rho\sigma \qquad (1)$$

$$\log(K/K_0) = \sigma \qquad (2)$$

In the 1950s, Brown noticed that the Hammett relation holds for the rates of electrophilic aromatic substitutions and solvolysis of substituted cumyl chlorides (**1**) only when the ring substituent is located in the *meta* position and defined new substituent constants (σ^+) based on the specific rates of solvolysis of cumyl chloride and its ring substituted homologues (k_0 and k, respectively) in 90% acetone−10% water (v/v) at 25 °C (eq 3).[1] The ρ^+ value of −4.54 was defined by using unsubstituted and *meta* substituted cumyl chlorides.[1]

$$(-1/4.54)\log(k/k_0) = \sigma^+ \qquad (3)$$

The so-called Brown−Okamoto σ^+ constants have made enormous contribution to organic chemistry. However, recent studies by Liu and co-workers indicated the possibility that the solvolysis of cumyl chloride and its substituted homologues may not be a k_c process, but one assisted by nucleophilic solvent participation in the activated complex for ionization.[2] Meantime, Richard et al. suggested that the Brønsted base type solvation to the methyl hydrogen atoms of the cumyl cation would be more important than the Lewis base type solvent intervention toward the cationic carbon.[3] It was cautioned that, whatever the mechanism of the nucleophilic solvent intervention may be, it would introduce an undesirable perturbation of the σ^+ values, especially if it varied with the substituent.[4]

The extent of nucleophilic solvent intervention in the cumyl solvolysis has been semiquantitatively examined on the basis of extended Grunwald−Winstein relations[2,4] and comparison of cation stability between the solution and gas phases.[3b] However, the effect of nucleophilic solvent intervention on the validity of the Brown−Okamoto σ^+ values has never been clarified.

Recently, we have studied the Grunwald−Winstein relationship for 2-chloro-2,4,4-trimethylpentane (**2**)[5a,b] and related systems,[5c] and reported that **2** is a tertiary alkyl k_c substrate that solvolyzes practically without either nucleophilic solvent intervention or neighboring group participation. The essential vanishment of nucleophilic solvent intervention has been ascribed to an efficient rear-side shielding effect of the neopentyl sub-

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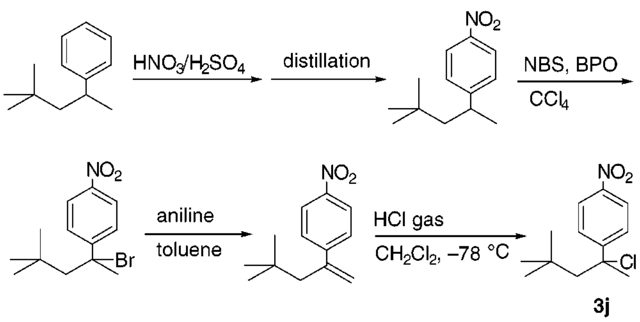
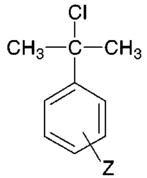
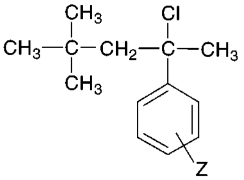
Scheme 1



stituent.[5] Consequently, we decided to examine whether the Hammett−Brown relation holds for the solvolysis of 2-aryl-2-chloro-4,4-dimethylpentanes (**3**) that were expected to behave as k_c substrates. We further wished to examine the additivity of the σ^+ values for the *m*-Cl and *m*-CF_3 substituents by using the solvolysis of **3k** and **3l**.

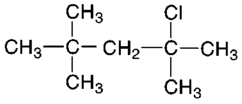


1



3

- **a**; Z=*p*-cyclopropyl
- **b**; Z=*p*-Me
- **c**; Z=*m*-Me
- **d**; Z=*p*-F
- **e**; Z=H
- **f**; Z=*p*-Cl
- **g**; Z=*m*-Cl
- **h**; Z=*m*-CF_3
- **i**; Z=*p*-CF_3
- **j**; Z=*p*-NO_2
- **k**; Z=3,5-Cl_2
- **l**; Z=3,5-$(CF_3)_2$



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{Cl}{\underset{CH_3}{C}}-CH_3$$

2

Results and Discussion

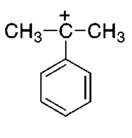
Synthesis. The chlorides **3** were prepared by hydrochlorination[6] of the corresponding alcohols that were derived by the Grignard reaction of 4,4-dimethyl-2-pentanone with arylmagnesium bromides. In some cases (*m*-Cl, *m*-CF_3, and 3,5-$(CF_3)_2$), the alcohols were dehydrated to olefins, which were then hydrochlorinated. The *p*-nitro derivative **3j** was prepared by the route shown in Scheme 1. The purities of freshly prepared **3e**−**l** were generally 70−97% by titration, the rest being the starting alcohol or olefins as estimated by ^{13}C NMR measurements. However, the chlorides **3a**−**d** were very unstable and formed large amounts of olefins during hydrochlorination; therefore, they were used directly for rate measurements immediately after evaporation of solvent.

Solvolysis Products. As a substrate for product study, *p*-trifluoromethyl derivative **3i** was selected because it could be prepared in a relatively pure state. The solvolysis was conducted on **3i** (0.02 mol L^{-1}) in 90% acetone in the presence of 2,6-lutidine (0.025 mol L^{-1}) for 10 half-lives at 25 °C. Analysis of the crude product by ^1H NMR showed the formation of 2-[(*p*-trifluoromethyl)phenyl]-4,4-dimethyl-2-pentanol (29%) and 2-[(*p*-trifluoromethyl)phenyl]-4,4-dimethyl-1-pentene (66%) as major products. The small signals at δ 2.16, which may be assigned to the methyl groups of (*Z*)- and (*E*)-2-[(*p*-trifluoromethyl)phenyl]-4,4-dimethyl-2-pentene, suggested their formation in 5%.

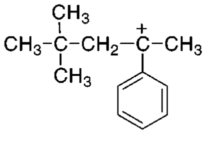
Table 1. Calculated Angles of Twisting (deg) from Coplanarity between the Aryl Ring and the sp^2 Plane of Carbocations 1e$^+$, 3e$^+$, and 4e$^+$ on the Basis of RHF/6-31G*

	angle of twisting (deg)		
source	**1e**$^+$	**3e**$^+$	**4e**$^+$
this work	5.0	3.2	24.5
ref 8b	5		24
ref 7			23.8

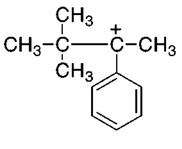
Calculated Structures of Carbocations. For the examination of Brown−Okamoto σ^+ constants, it is a prerequisite that the delocalization of positive charge to the *para* position is similar between the two systems **1** and **3** in the activated complex for ionization in solvolysis. To satisfy the prerequisite, the two systems having an identical substituent must attain similar coplanarity between the aryl ring and the sp^2 plane of the cationic center. Recently, experimental and theoretical studies on resonance demand in benzylic carbocations have been actively carried out by the groups of Liu and Tsuno.[7,8] We calculated the structure of unsubstituted carbocation **3e**$^+$ by using the RHF/6-31G* basis set.[9] For a comparative purpose, we repeated the previously reported calculations on **1e**$^+$ and **4e**$^+$; the twisted angles between the phenyl ring and the sp^2 cationic plane for the three carbocations are summarized in Table 1. The angles for **1e**$^+$ and **4e**$^+$ calculated in this work are 5.0° and 24.5°, respectively, and are in good agreement with reported values (5° [8b] and 24° [8b] or 23.8° [7]).[10] Notably, the twisted angle for **3e**$^+$ is 3.2°, which is even smaller than that for **1e**$^+$. This suggests that the system **3** is an appropriate model to examine the validity of σ^+ constants in the essential absence of nucleophilic solvent intervention. This notion was also supported by the *para*/*meta* solvolysis rate ratios for CH_3 and CF_3 substituents as an index for resonance contribution (see below).



1e$^+$



3e$^+$



4e$^+$

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Table 2. Brown−Okamoto σ^+ Constants and Specific Rate Constants for the Solvolysis of 2-Aryl-2-chloro-4,4-dimethylpentanes (3) in 90% Aqueous Acetone at 25 °C[a]

substituent	substrate	σ^+ [b]	k (s^{-1})
p-cycPr	**3a**	−0.462[c]	8.5×10^{-1} [d,e]
p-Me	**3b**	−0.311	1.9×10^{-1} [f,g]
m-Me	**3c**	−0.10	$(1.54 \pm 0.02) \times 10^{-2}$ [f]
p-F	**3d**	−0.073	$(1.35 \pm 0.02) \times 10^{-2}$ [f]
H	**3e**	0.000	$(7.27 \pm 0.02) \times 10^{-3}$ [f]
p-Cl	**3f**	0.11	$(2.06 \pm 0.01) \times 10^{-3}$ [h]
m-Cl	**3g**	0.399	1.18×10^{-4} [h]
m-CF_3	**3h**	0.520	2.75×10^{-5} [h]
p-CF_3	**3i**	0.612	1.16×10^{-5} [h]
p-NO_2	**3j**	0.790	2.00×10^{-6} [h]
3,5-Cl_2	**3k**		3.11×10^{-6} [h]
3,5-$(CF_3)_2$	**3l**		2.5×10^{-7} [d,i]

[a] The solvolysis was conducted in the absence of buffer. [b] Taken from ref 1, except the value for *p*-cycPr. [c] Ref 11. [d] Extrapolated from data at other temperatures. [e] Conductometric specific rate constants were 0.0172 s^{-1} (−20.0 °C), 0.0420 s^{-1} (−10.5 °C), and 0.111 s^{-1} (−0.4 °C). [f] Determined conductometrically. [g] Conductometric specific rate constants were 0.0253 s^{-1} (2.5 °C), 0.0532 s^{-1} (11.5 °C), 0.0806 s^{-1} (16.0 °C), and 0.0823 s^{-1} (16.2 °C). [h] Determined titrimetrically. [i] Titrimetrically determined specific rate constants were 4.43×10^{-6} s^{-1} (50.0 °C), 5.13×10^{-5} s^{-1} (75.0 °C), and 3.95×10^{-4} s^{-1} (100.0 °C).

Solvolysis Rates. The rates of solvolysis at 25 °C of 12 2-aryl-2-chloro-4,4-dimethylpentanes (**3**) were determined in 90% acetone−10% water (v/v), the solvent that had been used for determination of σ^+ values on the basis of solvolysis rates of **1**;[1] the specific rate constants are shown in Table 2. The specific rate constants of **3g**, **3i**, and **3l** in various solvents (Table 3) were determined to compare their Grunwald−Winstein type relations with those of the corresponding substituted cumyl chlorides **1** that had been reported by Liu.[2] The rates of **1l** were also measured in various solvents because of their absence in previous studies (Table 3). To examine the solvent effects on the ρ^+ value, the rates of **1h**, **1j**, **3h**, and **3j** in TFE were determined and summarized in Table 4. The significance of these rate data is discussed in the following sections.

Hammett−Brown Plot for the Rates in 90% Acetone. The 10 specific rate constants of solvolysis of **3** excluding **3k** and **3l** are plotted against Brown−Okamoto σ^+ constants in Figure 1. An excellent linear correlation with $\rho^+ = -4.51$ ($r > 0.999$) was obtained for a σ^+ range from −0.462[11] (*p*-cyclopropyl) to 0.790[1] (*p*-NO_2), suggesting that the Brown−Okamoto σ^+ values may be satisfactorily used in rear-side shielded, open-chain systems such as **3**. In other words, there is no worry about an undesirable perturbation of the σ^+ values by solvent nucleophilicity in the cumyl system, at least in the above σ^+ range.

Table 3. Specific Rate Constants for the Solvolysis of 3g, 3i, 3l, and 1l in Various Solvents at 25 °C[a]

	k [c] (s^{-1}), substituent and substrate			
solvent[b]	*m*-Cl, **3g**	*p*-CF_3, **3i**	3,5-$(CF_3)_2$, **3l**	3,5-$(CF_3)_2$, **1l**
100E	2.39×10^{-4} [d]	2.12×10^{-5} [d]	3.1×10^{-7} [e,f]	1.3×10^{-8} [e,g]
90E	1.79×10^{-3} [h]	1.98×10^{-4} [d]	1.66×10^{-6} [d]	9.1×10^{-8} [e,i]
80E	6.62×10^{-3} [h]	7.64×10^{-4} [h]	5.03×10^{-6} [d]	3.5×10^{-7} [e,j]
70E	1.92×10^{-2} [h]	2.01×10^{-3} [h]	1.24×10^{-5} [d]	9.74×10^{-7} [d]
60E	5.86×10^{-2} [h]	5.48×10^{-3} [h]		
100M		2.18×10^{-4} [d]		
90A	1.18×10^{-4} [d]	1.16×10^{-5} [d]	2.53×10^{-7} [d]	6.3×10^{-9} [k]
80A		1.00×10^{-4} [d]		
70A		4.70×10^{-4} [d]		
60A		2.16×10^{-3} [h]		
100T	2.7 [e,l]	2.5×10^{-1} [e,m]	1.43×10^{-3} [h]	6.67×10^{-6} [d]
80T−20E	3.1×10^{-1} [e,n]	3.07×10^{-2} [h]	1.74×10^{-4} [d]	1.26×10^{-6} [d]
60T−40E	4.67×10^{-2} [h]	4.24×10^{-3} [h]	2.61×10^{-5} [d]	2.9×10^{-7} [e,o]

[a] The specific rate constants for **3g**, **3i**, and **3l** in 90A were taken from Table 2. [b] E, M, A, and T denote ethanol, methanol, acetone, and 2,2,2-trifluoroethanol, respectively, and the preceding figures denote vol % of the organic components in aqueous mixtures at 25 °C except for T−E solvent systems. The figures given for the T−E systems indicate respective vol % at 25 °C. [c] Except for 90A, the rates were determined in the presence of 2,6-lutidine; 2×10^{-4} mol L^{-1} in T and T−E systems and 0.025 mol L^{-1} in the other solvents. Most of the data were obtained from duplicate runs within experimental errors of ±2% and ±0.5% in titrimetric and conductometric runs, respectively. [d] Determined titrimetrically. [e] Extrapolated from data at other temperatures. [f] Other specific rate constants were 7.26×10^{-6} s^{-1} (50.0 °C) and 1.03×10^{-4} s^{-1} (75.0 °C). [g] Other specific rate constants were 3.54×10^{-7} s^{-1} (50.0 °C), 6.07×10^{-6} s^{-1} (75.0 °C), and 7.18×10^{-5} s^{-1} (100.0 °C). [h] Determined conductometrically. [i] Other specific rate constants were 2.27×10^{-6} s^{-1} (50.0 °C), 3.17×10^{-5} s^{-1} (75.0 °C), and 3.36×10^{-4} s^{-1} (100.0 °C). [j] Other specific rate constants were 7.79×10^{-6} s^{-1} (50.0 °C) and 1.09×10^{-4} s^{-1} (75.0 °C). [k] ref 15. [l] Other specific rate constants were 0.0411 s^{-1} (−19.8 °C), 0.114 s^{-1} (−10.0 °C), and 0.191 s^{-1} (−5.0 °C). [m] Other specific rate constants were 0.0178 s^{-1} (0.6 °C), 0.0412 s^{-1} (8.0 °C), 0.0506 s^{-1} (10.0 °C), and 0.0892 s^{-1} (15.0 °C). [n] Other specific rate constants were 0.0251 s^{-1} (−0.4 °C), 0.0695 s^{-1} (9.1 °C), and 0.194 s^{-1} (20.0 °C). [o] Other specific rate constants were 5.91×10^{-6} s^{-1} (50.0 °C) and 7.60×10^{-5} s^{-1} (75.0 °C).

Table 4. Specific Rate Constants (k, s^{-1}) for the Solvolysis of 1h, 3h, 1j, and 3j in TFE at 25 °C[a]

	substituent	
substrate	*m*-CF_3 (**h**)	*p*-NO_2 (**j**)
1	3.56×10^{-3} [b]	3.24×10^{-5} [d]
3	5.8×10^{-1} [c]	6.87×10^{-3} [b]

[a] Determined in a single run conductometrically or titrimetrically in the presence of 2×10^{-4} or 0.025 mol L^{-1} 2,6-lutidine, respectively. [b] Determined conductometrically. [c] Extrapolated from conductometric specific rate constants 3.38×10^{-2} s^{-1} (−0.5 °C), 6.10×10^{-2} s^{-1} (4.5 °C), and 0.154 s^{-1} (12.5 °C). [d] Determined titrimetrically.

The good Hammett−Brown relation in the solvolysis of **3** indicates similarity in resonance demand in the activated complexes for **1** and **3**. This is experimentally substantiated by *p*-CF_3/*m*-CF_3 rate ratios[12] for **1** and **3** very close to each other, 0.375[13a] and 0.418, respectively, in 90% acetone at 25 °C. Similarly, the respective *p*-CH_3/*m*-CH_3 rate ratios are also close to each other at 13.0[13b] and 12.3. In contrast, the *p*-CF_3/*m*-CF_3 and *p*-CH_3/*m*-CH_3 rate ratios in a congested 2-aryl-2-chloro-3,3-dimethylbutane system (**4**) are 0.862 and 8.44, respectively, in 80% acetone at 45 °C,[14] showing the diminished sensitivity of the *para* substituents due to the decreased p-π overlap in the twisted activated complex.

Previously, one of the present authors (K.T.) reported that the σ^+ value for the 3,5-bis(trifluoromethyl)phenyl group was better described by 0.946 than by $2 \times \sigma^+_{m-CF_3}$ (1.040).[15] However, the determination depended on the

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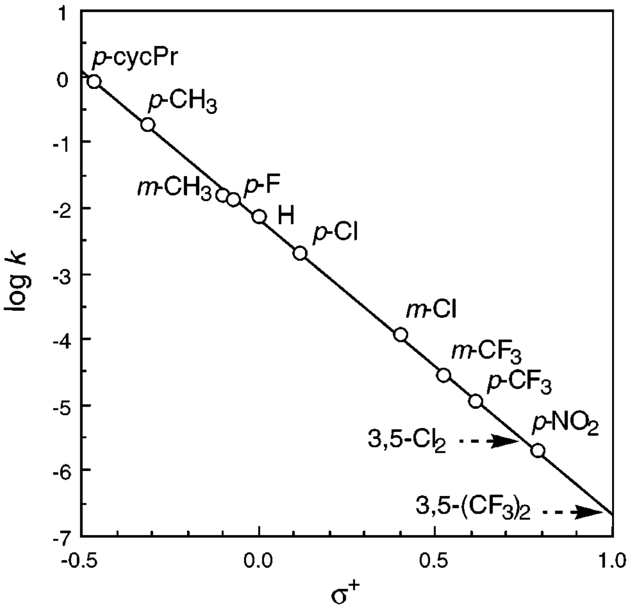

Figure 1. The Hammett–Brown relationship for the solvolysis of 2-aryl-2-chloro-4,4-dimethylpentanes (**3**) in 90% acetone at 25 °C: $\rho^+ = -4.51$; $r = 0.999$. The apparent σ^+ values of 3,5-Cl_2 and 3,5-$(CF_3)_2$ are evaluated to be 0.740 and 0.982, respectively, by placing log k values for **3k** (log $k = -5.507$) and **3l** (log $k = -6.602$) on the regression line.

estimated specific rate constant for the solvolysis of 3,5-bis(trifluoromethyl)cumyl chloride in 90% acetone at 25 °C that was obtained by extrapolation from data at 75 and 100 °C. In the present work, the additivity of the $\sigma^+_{m\text{-}CF_3}$ and $\sigma^+_{m\text{-}Cl}$ constants was examined by placing the log k values for **3k** and **3l** on the regression line in Figure 1 and by reading the corresponding abscissa values. In this way, the σ^+ values for the 3,5-bis(trifluoromethyl) and 3,5-dichloro substituents were determined to be 0.982 and 0.740, respectively, which are smaller than $2 \times \sigma^+_{m\text{-}CF_3}$ (1.040) and $2 \times \sigma^+_{m\text{-}Cl}$ (0.798) by 0.058 σ^+ unit in both cases. We recommend the use of the newly determined σ^+ values for the 3,5-$(CF_3)_2$ and 3,5-Cl_2 substituents in 90% aqueous acetone, especially when careful interpretation of rate data is required.

In this context, Creary reported a σ^+ value of 0.701 for the 3,5-dichloro substituents in EtOH.[16] This value is also smaller by 0.053 than $2 \times \sigma^+_{m\text{-}Cl}$ (0.754) using Brown–Okamoto's $\sigma^+_{m\text{-}Cl}$ in EtOH.[17] Similarly, Tsuji and coworkers estimate a σ^+ value for the 3,5-dichloro substituents in 80% aqueous acetone as 0.739,[18] which is practically identical to the present estimation of 0.740 in 90% aqueous acetone.

Solvent Effect on Reaction Constant ρ^+. The effect of solvent on the magnitude of ρ^+ in the solvolysis of the cumyl chloride system was studied by Brown in 1958 by changing the solvent, e.g., MeOH ($\rho^+ = -4.82$), EtOH ($\rho^+ = -4.67$), and i-PrOH ($\rho^+ = -4.43$), with 90% acetone ($\rho^+ = -4.54$) being standard.[17] Liu examined eight solvents in the solvolysis of 2-aryl-2-chloroadamantanes and obtained respective ρ^+ values,[2b] but little attention has been paid to the relation between the substrate structure, solvent, and magnitude of the ρ^+ values. Very recently, however, the Liu group has reported that the ρ^+ value for the solvolysis of substituted benzhydryl chlorides changes from −4.10 to −4.26 in nucleophilic solvents (EtOH, MeOH, their aqueous mixtures, and aqueous acetone) to −4.93 (60T–40E) to −5.12 (80T–20E) and that the nucleophilic solvent participation decreases the sensitivity of solvolysis rates to σ^+.[19] A similar trend has also been found in the solvolysis of 1-aryl-1-chloro-2,2-dimethylpropanes (1-aryl-1-*tert*-butylmethyl chlorides).[20]

Table 5. ρ^+ Values for the Solvolysis of 1 and 3 in Various Solvents at 25 °C[a,b]

	ρ^+		
solvent[c]	**1**	**3**	ρ^+(**3**)/ρ^+(**1**) ratio
100E	−4.67[d]	−4.95	1.06
90E	−4.90	−5.25	1.07
80E	−4.95	−5.41	1.09
70E	−5.11	−5.53	1.08
90A	−4.54[e]	−4.51	0.99
60T−40E	−5.46	−5.62	1.03
80T−20E	−5.81	−5.63	0.97
100T	−5.91	−5.63	0.95

[a] The ρ^+ values were obtained from m-Cl, p-CF_3, and 3,5-$(CF_3)_2$ points except for the cases in 100E, 90A, and 100T. As the σ^+ value for 3,5-$(CF_3)_2$, +0.982 was used; see text. [b] The correlation coefficient was greater than 0.997. [c] For notations, see footnote b to Table 3. [d] Ref 17. [e] Ref 1.

In Table 5 are summarized the ρ^+ values obtained for the systems **1** and **3** in eight solvents. Most of the ρ^+ values have been calculated from data derived from compounds containing three substituents, m-Cl, p-CF_3, and 3,5-$(CF_3)_2$. The large negative ρ^+ values in TFE, −5.91 and −5.63 for the solvolysis of **1** and **3**, respectively, reflect the decreased nucleophilic (or Brønsted base type) solvation by low nucleophilic solvent TFE. It is noted that the ratio in ρ^+ between **3** and **1** [ρ^+(**3**)/ρ^+(**1**)] is less than unity (0.95) in 100T, increases to 1.03 in 60T–40E, and becomes 1.07–1.09 in aqueous ethanol solvents. The ρ^+(**3**) less negative than ρ^+(**1**) in TFE would reflect an earlier transition state (TS) for **3** than for **1** because of a more congested destabilized ground state for **3**. The ρ^+ for solvolysis of **1** less negative than that for **3** in nucleophilic solvents would be ascribed to greater nucleophilic (or Brønsted base type) solvation in the activated complex for **1** that causes greater dispersion of positive charge to solvent.

Although Tsuji et al. reported that the change of solvents, such as aqueous acetone and aqueous ethanol, does not cause very serious deviation in the linearity of the Hammett–Brown plot,[18] we wish to caution against the use of the nitro substituent when TFE is used as solvent. As shown in Figure 2, the p-NO_2 data deviate downward by approximately 0.5 log k unit in the Hammett–Brown relation for both **1** and **3**. Probably, highly acidic TFE (pK_a 12.37[21]) solvates the anionic oxygen of the nitro group by hydrogen bonding, making it more electron-withdrawing. Similar rationalizations for the downward deviation of the solvolysis rates in TFE for the Grunwald–Winstein relations of 2-oxo and 3-oxo bridgehead compounds have been presented.[22] By the same

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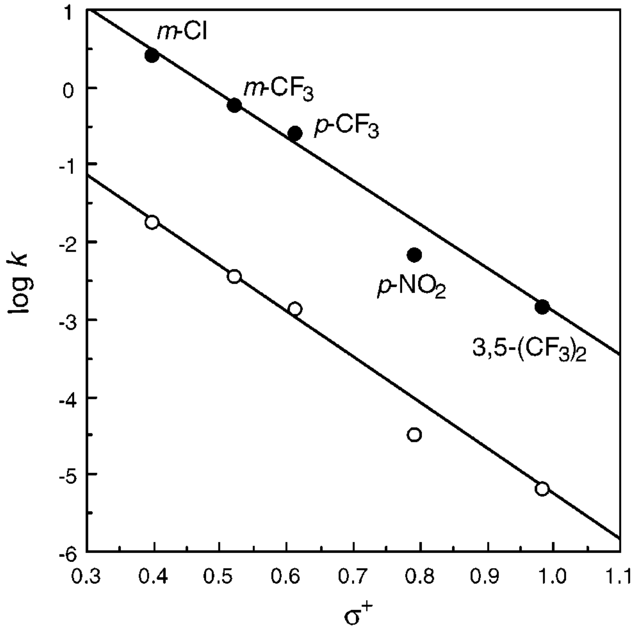


Figure 2. The Hammett–Brown relationships for the solvolysis of some substituted cumyl chlorides (**1**) and 2-aryl-2-chloro-4,4-dimethylpentanes (**3**) in TFE at 25 °C. The *p*-nitro points are not included in the regression analysis: open circle (**1**); solid circle (**3**).

token, the recent data reported by Liu and co-workers[19] for the solvolysis of substituted benzhydryl chlorides appears to show that *p*-nitrobenzhydryl chloride solvolyzes approximately 2 times slower in 60T–40E than expected from the rate in 80E.[23]

Comparison of Cation Stabilization by Solvent between 1 and 3. Liu and co-workers concluded that the solvolysis of cumyl chloride occurs with significant nucleophilic intervention of solvent,[2] whereas the Richard group suggested that Lewis base type stabilization of carbocations by nucleophilic solvation would be less significant than the "solvation of Brønsted acids and bases by formation of hydrogen bonds".[3] Both the Liu and Richard groups showed that cationic solvation of the cumyl system increases with increase in electron withdrawing ability of substituent.

Recently, we suggested that the placement of one or two neopentyl substituents in secondary and tertiary alkyl substrates not only effectively shields the rear side of the reaction center but also decreases the Brønsted acid–base type solvation.[5c] To demonstrate that **3** is a nearly limiting S_N1 system, the values of log *k* for **3i** were plotted against those for 2-chloro-2-[(*p*-trifluoromethyl)phenyl]adamantane[2b] (**5**) that had been reported by Liu (Figure 3). The good straight line shows that system **3** may be regarded as a limiting S_N1, open-chain aralkyl system.

Nucleophilic intervention by solvent was evaluated by the Liu group by comparing the downward deviations of the TFE (100T), 80T–20E, and 60T–40E points from the aqueous ethanol and aqueous acetone line for the logarithmic plot of the rate constants for the cumyl system against those for 2-chloro-2-(*m*-chlorophenyl)adamantane, i.e., Y_{BnCl}.[2] The greater deviations were interpreted as showing greater nucleophilic intervention by solvent. It appeared to us, however, that it would be more appropriate to compare the rates between the above two systems **1** and **3** having the same substituent. In the present work, we compared the rates of the cumyl system[2f] **1** with those of **3** for same substituents, *m*-Cl, *p*-CF_3, and 3,5-$(CF_3)_2$. Figure 4 shows the plots of $\log(k/k_0)$ between the two systems for these substituents, where k_0 is the specific rate constant for solvolysis in 80% ethanol. Apparently, the downward deviation of less nucleophilic solvents containing TFE becomes larger in the order *m*-Cl, *p*-CF_3, and 3,5-$(CF_3)_2$. Liu and co-workers showed that replacement of one methyl group of **1e** with an isopropyl group essentially eliminates the nucleophilic solvent intervention, but it revives for the *m*-chloro derivative.[24] The present result is consistent with their conclusion that the nucleophilic intervention by solvent in the cumyl and related systems increases as the carbocation becomes more electron-demanding.[2] Analyses of the rate data in Table 3 for the solvolysis of **3g**, **3i**, **3l**, and **1l** and reported data[2e,f] for **1g** and **1i** by the extended Grunwald–Winstein relationship, $\log(k/k_0) = mY_{BnCl} + lN_{OTs}$, show that **3** compounds are less nucleophilically assisted than **1** compounds by 0.2–0.4 *l* unit.[25] However, present data do not permit evaluation of the relative

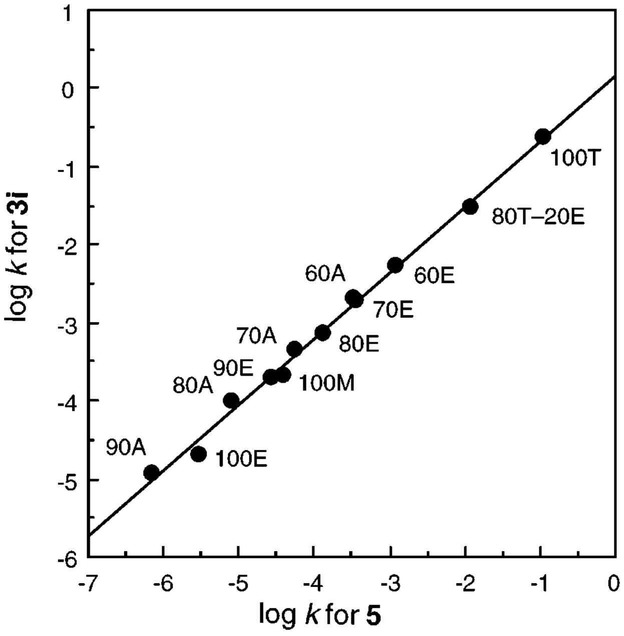
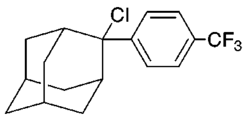


Figure 3. A plot of log *k* values for 2-chloro-2-(*p*-trifluoromethyl)phenyl-4,4-dimethylpentane (**3i**) against those for 2-chloro-2-(*p*-trifluoromethyl)phenyladamantane (**5**) for solvolysis in various solvents at 25 °C. For the specific rate constants for **3i** and **5**, see Table 3 and ref 2b, respectively.



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(22) (a) Yoshida, M.; Takeuchi, K. *J. Org. Chem.* **1993**, *58*, 2566. (b) Takeuchi, K.; Yoshida, M.; Kurihara, Y.; Kinoshita, T.; Kitagawa, T. *J. Org. Chem.* **1994**, *59*, 6459. (c) Takeuchi, K.; Ohga, Y.; Yoshida, M.; Ikai, K.; Shibata, T.; Kato, M.; Tsugeno, A. *J. Org. Chem.* **1997**, *62*, 5696.

(23) This conclusion was drawn on the basis of the downward deviation of the *p*-NO_2 data point in a plot of log *k* in 60T–40E vs log *k* in 80E for the solvolysis of *p*-CH_3, (H), *m*-Cl, *m*-CF_3, and *p*-NO_2 benzhydryl chlorides by using the reported data;[19] see Figure S1 in Supporting Information.

(24) Liu, K.-T.; Chen, P.-S. *J. Chem. Res., Synop.* **1994**, 310.

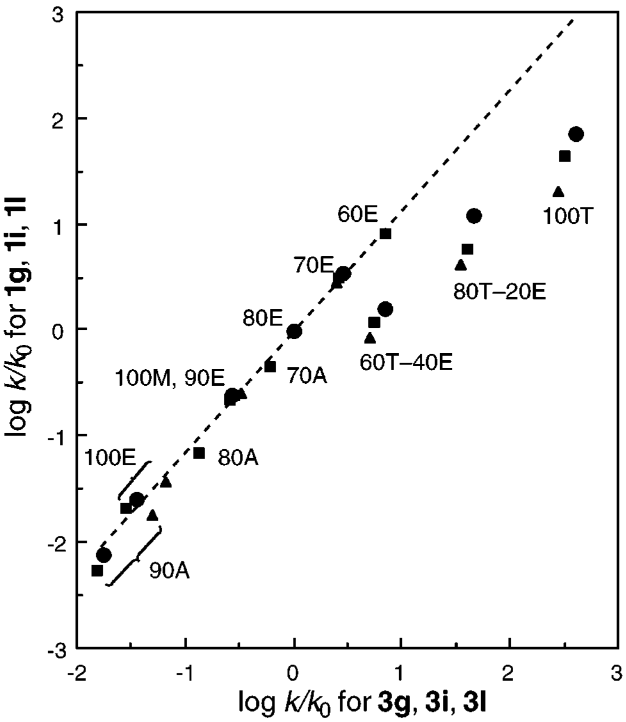

Figure 4. Plots of log(k/k_0) values for **1g**, **1i**, and **1l** versus those for **3g**, **3i**, and **3l**, respectively, for solvolysis in various solvents at 25 °C. For the specific rate constants, see Table 3 for **3g**, **3i**, **3l**, and **1l** and ref 2f for **1g** and **1i**: solid circle (**1g** vs **3g**); solid square (**1i** vs **3i**); solid triangle (**1l** vs **3l**).

importance of the Brønsted base type solvation to the methyl hydrogen atoms of the cumyl cation and the Lewis base type solvent intervention toward the cationic carbon.

Experimental Section

Boiling points are uncorrected. 2,6-Lutidine was distilled over CaH_2. Other commercially available reagents were reagent grade quality and were used as received. Solvolysis solvents were prepared as previously described.[27] 2-Aryl-2-chloropropanes, **1h**,[13a] **1j**,[28] and **1l**,[15] were prepared following the reported procedures. The ^{13}C NMR and boiling point data for 2-aryl-4,4-dimethyl-2-pentanols (**3-OH**) are summarized in Supporting Information. Preparation of 2-chloro-2-(*p*-nitrophenyl)-4,4-dimethylpentane (**3j**) and ^{13}C NMR data for 2-aryl-2-chloro-4,4-dimethylpentanes (**3**) are also given in Supporting Information.

2-Chloro-2-[(*p*-trifluoromethyl)phenyl]-4,4-dimethylpentane (3i) by Hydrochlorination of Alcohol (3i-OH); Typical Procedure. The alcohol, 2-[(*p*-trifluoromethyl)phenyl]-4,4-dimethylpentanol (**3i-OH**), was prepared in 63% yield by treating 4,4-dimethyl-2-pentanone (4.97 g, 43.4 mmol) with *p*-(trifluoromethyl)phenylmagnesium bromide prepared from *p*-bromobenzotrifluoride (11.4 g, 50.7 mmol) and Mg turnings (1.30 g, 53 mmol) in diethyl ether: bp 58−59 °C at 0.18 mmHg. **3i-OH** (3.98 g) was treated with dry HCl in pentane at −78 °C for 30 min, the reaction mixture was dried over $CaCl_2$, and the solvent was evaporated to give a yellow oil that was found to contain **3i** in 97% and 2-[(*p*-trifluoromethyl)phenyl]-4,4-dimethyl-1-pentene in 3%. The mixture was used for rate and product studies.

2-Chloro-2-(*m*-chlorophenyl)-4,4-dimethylpentane (3g) by Hydrochlorination of Olefin; Typical Procedure. The corresponding alcohol, 2-(*m*-chlorophenyl)-4,4-dimethylpentanol (**3g-OH**), was prepared in 79% yield by treating 4,4-dimethyl-2-pentanone (1.93 g, 13.4 mmol) with *m*-chlorophenylmagnesium bromide prepared from *m*-bromochlorobenzene (3.57 g, 18.6 mmol) and Mg turnings (0.58 g, 24 mmol) in diethyl ether: bp 74−76 °C at 0.23 mmHg. **3g-OH** (3.17 g) was mixed with $KHSO_4$ (3.26 g), and the mixture was heated in a distillation flask to give essentially pure 2-(*m*-chlorophenyl)-4,4-dimethyl-1-pentene (2.86 g) as a colorless liquid in 83% yield: bp 68−69 °C at 0.28 mmHg. The olefin was treated with dry HCl in CH_2Cl_2 at 0 °C to give **3g** as a pale yellow oil. A ^{13}C NMR measurement showed the purity of **3g** to be 84%, the rest being the starting olefin.

Rate Studies. The rates of solvolysis were determined titrimetrically or conductometrically following previously reported procedures.[27] The chlorides obtained by hydrochlorination of the corresponding tertiary alcohols or olefins were used without further purification because of the instability of the chlorides. The first-order plots were satisfactorily linear until 80−90% conversion.

Product Studies for the Solvolysis of 3i. A solution of **3i** (279 mg, 10.0 mmol) in 90% (v/v) aqueous acetone (50.0 mL) containing 0.025 mol L^{-1} of 2,6-lutidine was kept at 25.0 °C in a constant-temperature bath for 168 h (10 half-lives). Most of the acetone was rotary evaporated, and the residue was extracted with diethyl ether. The organic layer was washed with 5% aqueous HCl and 10% aqueous Na_2CO_3 and dried ($MgSO_4$). After evaporation of the solvent, the residue was analyzed by ^1H NMR (270 MHz, $CDCl_3$) to show the presence of 2-[(*p*-trifluoromethyl)phenyl]-4,4-dimethyl-2-pentanol (**3i-OH**) (29%) and 2-[(*p*-trifluoromethyl)phenyl]-4,4-dimethyl-1-pentene (66%). The weak absorptions at δ 2.16 suggested that (*Z*)- and (*E*)-2-[(*p*-trifluoromethyl)phenyl]-4,4-dimethyl-2-pentenes had been formed in 5%.

Computational Studies. Ab initio molecular orbital calculations were carried out with the Gaussian 94 program on a CRAY T94/4128 computer. The geometries were fully optimized at the RHF/6-31G* level for all the molecules treated.

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Supporting Information Available: ^{13}C NMR and boiling point data for 2-aryl-4,4-dimethyl-2-pentanols (**3-OH**), synthetic procedures for 2-chloro-2-(*p*-nitrophenyl)-4,4-dimethylpentane (**3j**), ^{13}C NMR data for some 2-aryl-2-chloro-4,4-dimethylpentanes (**3e−l**), a plot of log *k* in 60T−40E vs log *k* in 80E for the solvolysis of various benzhydryl chlorides (Figure S1), and some analysis results for the extended Grunwald−Winstein relation. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) For detailed analysis results, see Supporting Information. The use of N_T in place of N_{OTs} led to a similar conclusion. For Y_{BnCl}, N_{OTs}, and N_T values, see refs 2b, 26, and 4a, respectively.

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