# Structural modification and solvent interactions in solvolytic reactions of open-chain compounds

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*Abstract*: The Grunwald–Winstein type analyses with respect to $Y_{Cl}$ scale on the specific rates of solvolysis of extremely crowded tertiary alkyl chlorides having a neopentyl or a (1-adamantyl)methyl group at the reaction center show that they behave as $k_c$ substrates. The neopentyl group is more effective in backside shielding than a tertiary butyl group. There are now many unprecedented examples that show downward dispersions of aqueous ethanol and aqueous acetone data points relative to fluorinated solvents in the Grunwald–Winstein type relations. The principal cause for such behavior is attributed to diminished rates in water relative to those in nonaqueous solvents. In the solvolyses of $(t\text{-BuCH}_2)\text{Et}_2\text{CCl}$ and $(t\text{-BuCH}_2)_2\text{MeCCl}$ (**9**), the deviated aqueous ethanol data exhibit a downward convex, enhancing the downward deviations. Secondary mesylates, $(t\text{-BuCH}_2)_2\text{CHOMs}$ and $(t\text{-BuCH}_2)(1\text{-AdCH}_2)\text{CHOMs}$, and even 1-bromo-3,5,7-triisopropyladamantane behave similarly to congested tertiary open-chain alkyl chlorides. In the solvolysis of **9** in aqueous ethanol, the product selectivity with respect to ethanol is considerably increased compared with the case of *tert*-butyl chloride. Steric and hydrophobic perturbation to solvation in the ground state and intermediate would provide a reasonable explanation.

## INTRODUCTION

Solvolytic reactions have played a major role in the advancement of carbocation chemistry during the 20th century. The major methodologies in solvolysis studies are the linear free-energy relationship (LFER) and product analysis. They provide us with information on the stability, structure, and solvent interaction of the transition state and intermediate carbocations. On the other hand, spectroscopic observation of carbocations, X-ray crystallography, and measurements of thermodynamic stabilities under stable ion conditions and in the gas phase unveiled vivid structural characteristics of carbocations.

Despite the splendorous progress in carbocation chemistry in this century, the microscopic role of solvent molecules in the ionization step of solvolysis substrates has not necessarily been clarified. Among various LFER equations and solvent parameters the most widespread relation is that proposed by Grunwald and Winstein (Eq. 1) (1,2).

$$\lg(k/k_0)_{RX} = mY + c \qquad (1)$$

In Eq. 1, $k$ and $k_0$ are the specific rates of solvolysis at 25.0 °C of RX in a given solvent and in 80% ethanol, respectively, $m$ is the sensitivity of the specific rate to changes in solvent ionizing power ($Y$), and $c$ is the intercept. Originally, the $\lg(k/k_0)$ values for *tert*-butyl chloride (**1**) solvolysis were taken as the $Y$ scale, but the finding of a possibility for the presence of nucleophilic solvent participation in the ionization step of **1** led Bentley and Carter to propose the $Y_{Cl}$ scale by using 1-chloroadamantane (**2**) in place of **1** (3) At the present time, various $Y_X$ scales for leaving groups (X) are available on the basis of solvolysis rates of

1-adamantyl or 2-adamantyl substrates whose backside is severely blocked to $S_N2$ type attack or nucleophilic solvent participation (2b). The generalized relation is represented by Eq. 2.

$$\lg(k/k_0)_{RX} = mY_X + c \qquad (2)$$

Although detailed discussions have been the subject of review articles (2,4), it seems to the present author that the extended Grunwald–Winstein relations including nucleophilic parameter $N$ ($N_{OTs}$, $N_T$) (Eq. 3) (2b,4a,5) and aromatic ring parameter $I$ (Eq. 4) (6) are recommended for probing the roles of solvents in solvolytic reactions. However, these equations do not include a *cation solvation* term, and it is treated as a part of *nucleophilic solvent participation*.

$$\lg(k/k_0)_{RX} = lN + mY_X + c \qquad (3)$$

$$\lg(k/k_0)_{RX} = lN + mY_X + hI + c \qquad (4)$$

Recently, specific rates of solvolysis of several extremely crowded alkyl derivatives have been examined by Eq. 2, and its limitation has been suggested (7,8). The current information regarding more recent results and possible causes will be discussed herein.

## SOLVOLYTIC BEHAVIOR OF VARIOUS CROWDED ALKYL DERIVATIVES

### RMe₂CCl [R = Me (1), t-Bu (3), Pr (4), i-Bu (5), t-BuCH₂ (6), 1-AdCH₂ (7)] system

The Grunwald–Winstein relations for the solvolysis of **1** and **3** have been carefully analyzed by Kevill (9) and Liu (10). On the other hand, the solvolyses of **4** and related alkyl chlorides **5–7** having branching at the γ position have been subjected to detailed analyses only recently (7,8). Figure 1 shows the lg $k$–$Y_{Cl}$ correlations in representative solvents for the six tertiary alkyl chlorides (7,11).
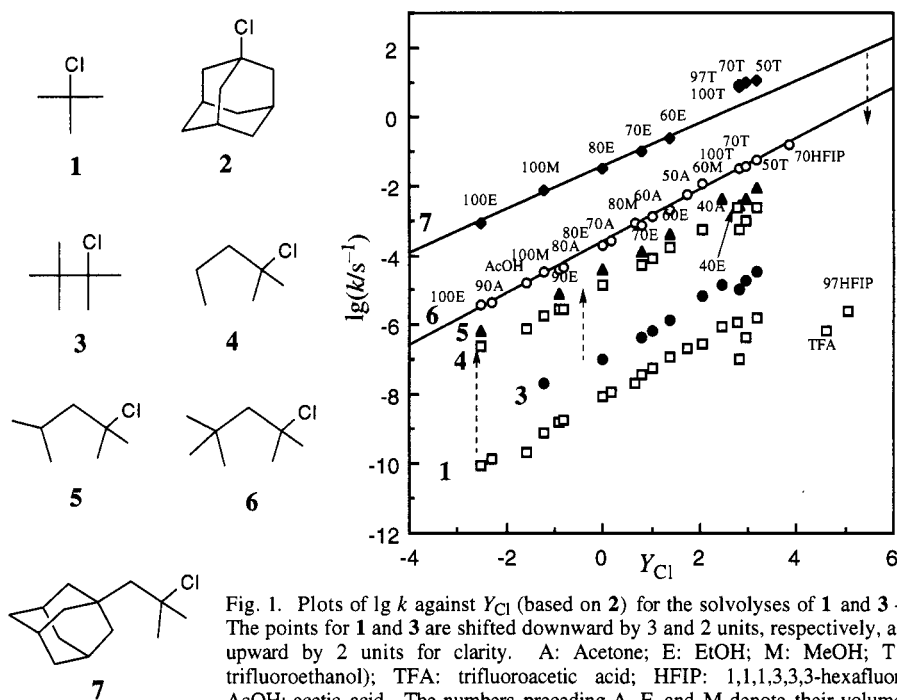


Fig. 1.  Plots of lg $k$ against $Y_{Cl}$ (based on **2**) for the solvolyses of **1** and **3 – 7** at 25 °C. The points for **1** and **3** are shifted downward by 3 and 2 units, respectively, and those for **7** upward by 2 units for clarity.  A: Acetone; E: EtOH; M: MeOH; T: TFE (2,2,2-trifluoroethanol); TFA: trifluoroacetic acid; HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol; AcOH: acetic acid. The numbers preceding A, E, and M denote their volume % at 25 °C, and those for T and HFIP mean their weight %, all in aqueous mixtures. $m$: 0.74 for **6**.

The downward dispersions of the data points for fluorinated solvents in the solvolysis of *tert*-butyl chloride (**1**) have been ascribed to the enhanced rates in more nucleophilic solvents such as ethanol, methanol, and their aqueous mixtures (3). Application of this notion to the behavior of the other chlorides suggests that the nucleophilic solvent participation still operates in **3**, **4**, and **5**, because the data points for 100% TFE (100T) and aqueous TFE fall below the aqueous ethanol lines. However, the data for **6** in fluorinated solvents [100T, 70T, 50T, and 70HFIP] fall on a straight line defined by the other aqueous organic solvents, indicating that the nucleophilic solvent participation essentially vanishes in the solvolysis of **6**. The results suggest that the neopentyl group in **6** is a better backside-shielding substituent than the *tert*-butyl group in **3**. On proceeding to **7**, 100T, 97T, and aqueous TFE data points are located above the aqueous ethanol line. This type of deviation could reasonably be interpreted by postulating smaller extents of *cation solvation* than the standard compound 1-chloroadamantane (**2**). Although the major products from **6** and **7** are olefins, the compositions are similar; therefore, the predominant elimination would not be concerned with the upward deviations of the data points for fluorinated solvents, which is not the case in **6**.
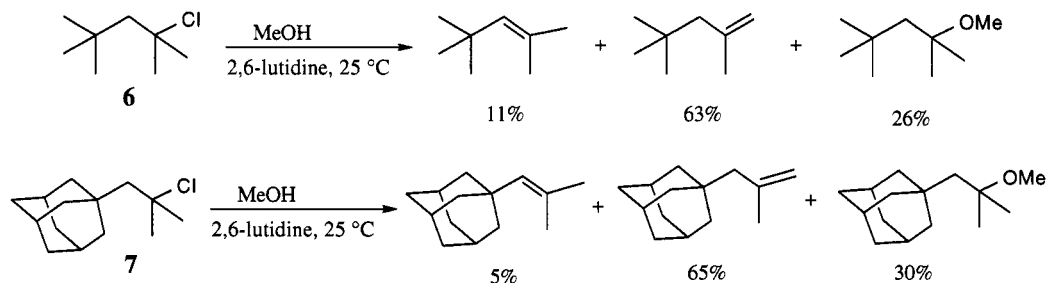


Analyses of the solvolysis rate data by using Eq. 3 including $N_T$ (defined on the basis of the solvolysis of *S*-methyldibenzothiophenium ion) (5) and $Y_{Cl}$ give *l* values decreasing in the order **1** (0.38±0.03, *n*=46) > **4** (0.15±0.03, *n*=14) > **3** (0.10±0.04, *n*=10) ≈ **5** (0.09±0.04, *n*=9) > **6** (0.00±0.02, *n*=18) > **7** (−0.13±0.06, *n*=9) (7b, 11), as expected from the dispersion patterns in Fig. 1.

The rate data in this study also give an important insight into the magnitude of the relief of B-strain involved in the solvolysis of **6**. Brown and co-workers compared the rate of **6** with that of **1** in 80% ethanol (80E) at 25 °C and obtained **6/1** rate ratio of 21 (12). The enhanced rate of **6** was attributed to the acceleration of solvolysis of **6** by B-strain in the ground state. Since nucleophilic solvent participation and/or cation solvation are significant in **1**, the **6/1** rate ratio should be investigated by using a solvent with a nucleophilicity as low as possible. The **6/1** rate ratio in TFE is 275, and estimated rate ratios in TFA and 97HFIP are 950 and 520, respectively (7). Evidently, the previously assigned B-strain effect for **6** as measured by the solvolysis rate ratio has been underestimated by a factor of at least 40.

## (*t*-BuCH₂)Et₂CCl (8), (*t*-BuCH₂)₂MeCCl (9), (*t*-BuCH₂)₂CHOMs (10), and (*t*-BuCH₂)(1-AdCH₂)CHOMs (11)

The neopentyl (*t*-BuCH₂) group in **6** has been shown to shield the backside of the cationic carbon more effectively than the *t*-butyl group in **3**. The more bulky and rigid (1-adamantyl)methyl group in **7** appears to make **7** less nucleophilically assisted (or rather less solvated on the cation side) than **6**, and even than 1-chloroadamantane (**2**). The effects of two substituents have been more extensively investigated by subjecting the sterically congested tertiary and secondary substrates **8**–**11** to solvolysis studies (8,13). The lg *k* values for **8** and **9** are plotted against $Y_{Cl}$ (Fig. 2) and those for **10** and **11** against $Y_{OTs}$ (Fig. 3).
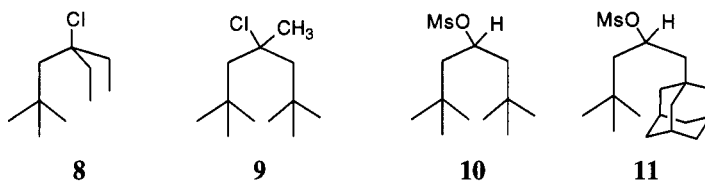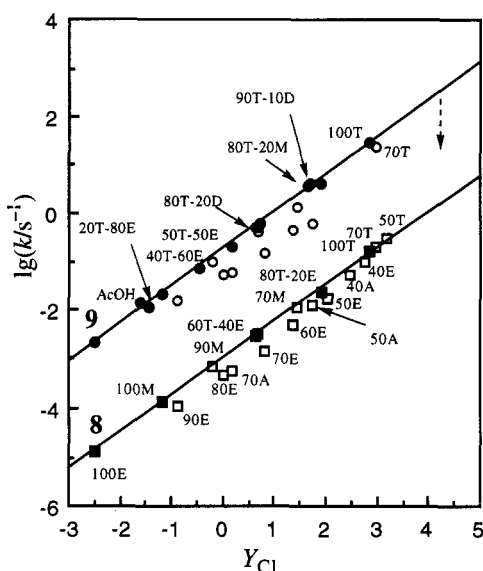
Fig. 2. Plots of lg $k$ against $Y_{Cl}$ for the solvolyses of 8 and 9 at 25 °C. The points for 9 are shifted upward by 1 unit for clarity. D: DMSO. For the other notations of solvents see the caption to Fig. 1. The lines are drawn for nonaqueous points; $m$: 0.75 (8), 0.77 (9).

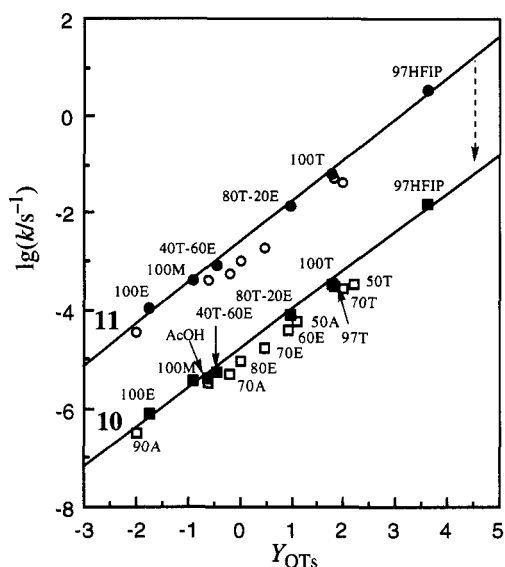Fig. 3. Plots of lg $k$ against $Y_{OTs}$ for the solvolyses of 10 and 11 at 25 °C. The points for 11 are shifted upward by 2 units for clarity. For the notation of solvents see caption to Fig. 1. The lines are drawn for nonaqueous points; $m$: 0.80 (10), 0.84 (11).

As expected from the behavior of 7 in Fig. 1, all the congested alkyl substrates 8–11 show unprecedented behavior in the Grunwald–Winstein type plots. First, the lg $k$ values for nonaqueous solvents (97HFIP, 100T, 100E, 100M, AcOH, T–E, T–M, T–D) are well accommodated to a single straight line in each case. Second, the aqueous ethanol and aqueous acetone points show downward deviations. Third, the deviations are larger for more crowded substrates, i.e., 9 > 8 and 11 > 10. Fourth, perhaps most important, aqueous ethanol points show a downward convex for the solvolyses of 8 and 9, whereas aqueous methanol points are linearly correlated. However, in order to probe the contrast in the behavior of aqueous ethanol and aqueous methanol solvents, more rate data would be required for the solvolyses of 7, 10, and 11.

## Origins of dispersions of data points for aqueous organic solvents

The lg $k$–$Y_{Cl}$ correlation for *tert*-butyl chloride (1) was examined by Bentley and Carter in 1982 (3). They pointed out a downward dispersion of the points for fluorinated solvents such as 97HFIP, TFA, TFE, and TFE–H$_2$O. The faster rates of solvolysis of 1 in aqueous organic solvents such as EtOH–H$_2$O, MeOH–H$_2$O, TFE–H$_2$O, and acetone–H$_2$O than expected from fluorinated solvent data points were ascribed to nucleophilic assistance to ionization in aqueous solvent mixtures. However, the lg $k$–$Y_{Cl}$ correlation in anhydrous protic solvents has not been examined. Figure 4 shows that the data points are classified into two linear relations, i.e., aqueous solvent mixtures and nonaqueous protic solvents. It should be noted that, with the exception of the formic acid and methanol points, nonaqueous protic solvents, such as ethanol, acetic acid, TFE, TFA, 97HFIP, TFE–EtOH, TFE–MeOH, and TFE–DMSO, give a single linear relation. The upward deviation of the data points for aqueous solvent mixtures is obviously caused by the very fast rate of 1 in water. Clearly, the problem is focused on the question of why water accelerates dramatically the solvolysis of *tert*-butyl chloride as compared with 1-chloroadamantane. It is also noted that the EtOH–H$_2$O points give rise to a slightly upward convex line. As pointed out in Figs. 2 and 3, the nonaqueous solvents exhibit linear relations in the Grunwald–Winstein type plots for 8–11. The modes of behavior for the four tertiary alkyl chlorides, 1, 6, 8, and 9, are summarized as a somewhat exaggerated sketch in Fig. 5. The

solvolysis rates in water for **6, 8**, and **9** are difficult to determine by direct rate measurements because of their low solubilities; therefore, their specific rates in water were estimated by extrapolation of nice linear relations for aqueous methanol data points to $Y_{Cl} = 4.57$ (3). As noted with respect to the plot for **9** in Fig. 2, the data points for both MeOH–H$_2$O and EtOH–H$_2$O fall below the nonaqueous solvent line. This suggests that **9** may be less nucleophilically assisted than the standard 1-chloroadamantane (**2**).
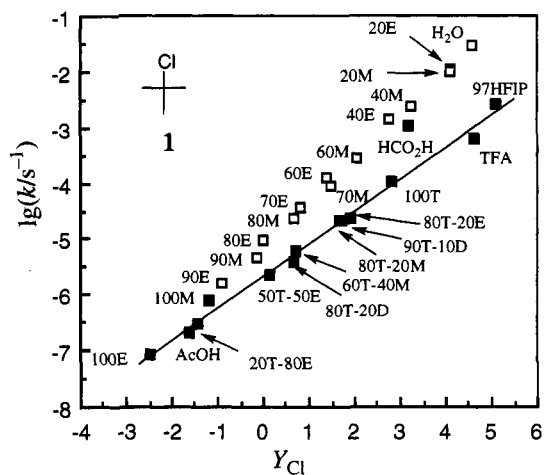


Fig. 4. Plots of lg $k$ values against $Y_{Cl}$ for solvolyses of *tert*-butyl chloride (**1**). For the notation of solvents, see Figs. 1 and 2. *m*: 0.58 for nonaqueous solvents except for 100M and HCO$_2$H.
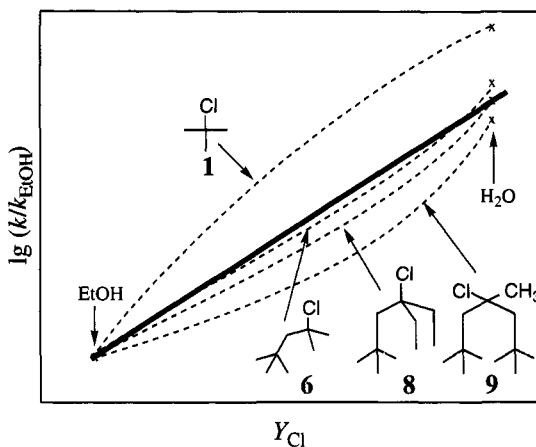
Fig. 5. A sketch of the Grunwald–Winstein relationship with respect to $Y_{Cl}$ for the solvolyses of **1, 6, 8**, and **9** in nonaqueous solvents (solid line) and EtOH–H$_2$O (dotted line).

1-Chloroadamantane cannot be attacked by a nucleophile from the backside. Therefore, the result that **2** is more susceptible to solvent nucleophilicity than **9** may be interpreted as a sign that the former is more strongly solvated than the latter on the cation side in the transition state of ionization. Recently, Richard and co-workers pointed out that Brønsted base-type solvation to β-hydrogens would be more important than nucleophilic assistance toward carbenium carbon in the ionization step of cumyl substrates (14). According to Monte Carlo and RISM calculations on hydration of a *t*-Bu$^+$Cl$^-$ ion pair, the average primary hydration number is about 1 for carbenium carbon, but it amounts to 3 for each methyl group (15). The latter type of solvation to β-hydrogens in the transition state of ionization of **9** should be severely blocked owing to the presence of bulky *tert*-butyl groups.

The curved plots that are specifically observed for aqueous ethanol solvents in the solvolysis of crowded substrates (Figs. 2, 3, 5) call for caution and place a limitation on the use of this solvent system. Aqueous methanol is a good solvent system in this respect, but poor solubilities of substrates restrict its wide use. Several factors could be behind the behavior of aqueous ethanol to give curvatures, including changing cluster structure, possibility of solvent sorting or formation of water pools, difference in ground state solvation, and even mechanistic difference between the crowded alkyl systems and standard 1-chloroadamantane (**2**).

Very recently, Kevill applied Eq. 4 to the rate data for **9** and **10**, and suggested a possibility that their behavior could originate from diminished ion-pair return (16). However, it may not be possible to rationalize the almost normal behavior of aqueous methanol solvents (Fig. 2).

Phenomenologically, the marked curvatures in the plots of aqueous ethanol data (Figs. 2, 3, 5) stem from significant deviations from linearity in the lg $k$ vs. water mole-fraction ($f_{H2O}$) plots (Fig. 6). More comprehensible plots are given in Fig. 7, where the deviations (Δlg $k$) in Fig. 6 are plotted against $f_{H2O}$. The deviation increases in the order **1 < 2 ≤ 6 < 8 < 9**. On the other hand, in similar plots for aqueous

methanol, the five compounds show essentially the same small deviation of about –0.2 when compared with –0.6 ~ –1.1 in aqueous ethanol. Presumably, the dissimilar behavior between the two solvent systems would be concerned with markedly different compositions of clusters (17), which may cause a different mode of interaction with both the ground state and the transition state for ionization. In any event, because of the *nonlinear* behavior of aqueous ethanol with the structural change of substrates, linear regression analyses of the rate data for crowded compounds such as **8**, **9**, and **10** based on Eqs. 3 and 4 would be misleading.
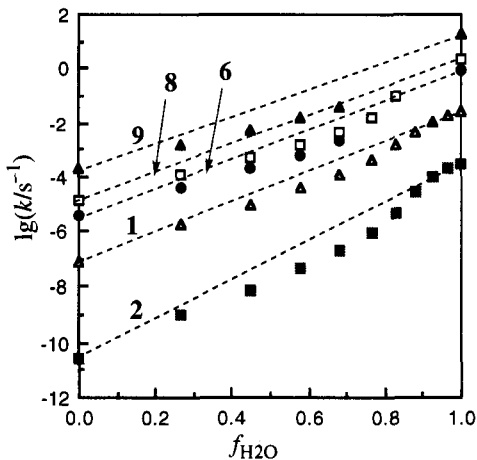


Fig. 6. Plots of lg $k$ against mole fraction of water in the solvolysis of **1**, **2**, **6**, **8**, and **9** in EtOH–$H_2O$ at 25 °C.
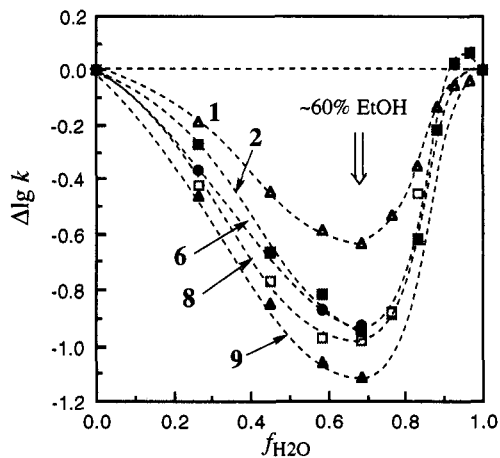
Fig. 7. Plots of deviations of lg $k$ from linear line in Fig. 6 against mole fraction of water.

## Solvent selectivity in the solvolysis of 9 in aqueous ethanol and aqueous methanol

The major reason for the downward deviations of the water and aqueous ethanol data points for extremely crowded alkyl substrates in Figs. 2 and 3 is still controversial (8,16,18b). We have postulated that a smaller extent of Brφnsted base-type solvation in congested substrates than in the standard 1- and 2-adamantyl substrates in the transition state of ionization could rationalize the results (8). In particular, the greater extent of rate retardation for **9** than for 1-chloroadamantane (**2**) in aqueous ethanol (Fig. 7) suggests the possibilities of greater degrees of *hydrophobic solvation by ethanol* in the ground state and/or smaller degrees of *hydration* in the transition state for ionization of **9**. If this is the case, and if the ion pair intermediate of simple tertiary systems undergoes direct reaction with a molecule of solvent within the solvation shell that is present at the time of its formation before solvent reorganization occurs (18a), the ether/alcohol (**9-OEt/9–OH**) product ratio is expected to be larger than the case of less congested compounds. Although the major products are olefins (8), it is possible to determine the solvent selectivity in a substitution reaction. In 80% ethanol in the presence of 2,6-lutidine at 25 °C, **9–OEt** and **9–OH** were formed in a ratio of 77/23 and in a combined yield of 4.3% (19). In contrast, it was reported in 1938 that *tert*-butyl chloride (**1**) afforded **1-OEt** and **1-OH** in a ratio of 33/67 under similar conditions (20). The dramatic increase in the ether/alcohol product ratio for **9** as compared with **1** is consistent with the interpretation in rate studies. The result in 90% ethanol is in accord with the data in 80% ethanol. Interestingly, the ether/alcohol product ratio in aqueous methanol for **9** is similar to that for **1** (19).

## 1-Bromo-3,5,7-trimethyladamantane (13) and 1-bromo-3,5,7-triisopropyladamantane (14)

The standard compounds for $Y_X$ values are 1- and 2-adamantyl derivatives that give only substitution products in solvolysis. On the other hand, the crowded alkyl compounds that show unusual Grunwald–Winstein relations give olefins as major products. The marked difference in product pattern might be an

indication for different mechanisms including significant difference in ion pair return (16) and unusual four-center type elimination reaction (18). This question may be approached by evaluating the solvolysis rates of 1-bromo-3,5,7-trimethyladamantane (13) and 1-bromo-3,5,7-triisopropyladamantane (14) in comparison with 1-bromoadamantane (12) (19). Figure 8 shows the Grunwald–Winstein type plots by using tentative rate data for the solvolyses of 13 and 14 with respect to the $Y_{Br}$ scale (2b,3) that is based on the solvolysis rates of 12. Although more data points would be required for a detailed discussion, an upward deviation of the data points for both 13 and 14 in fluorinated solvents is obvious when compared with the aqueous ethanol lines. The $m$ values for the solvolysis in aqueous ethanol obtained by using the rate data between 100% and 50% ethanol are 0.87 and 0.61 for 13 and 14, respectively. Both 13 and 14 give the same $m$ value (0.98) in nonaqueous solvents and only bridgehead substitution products.
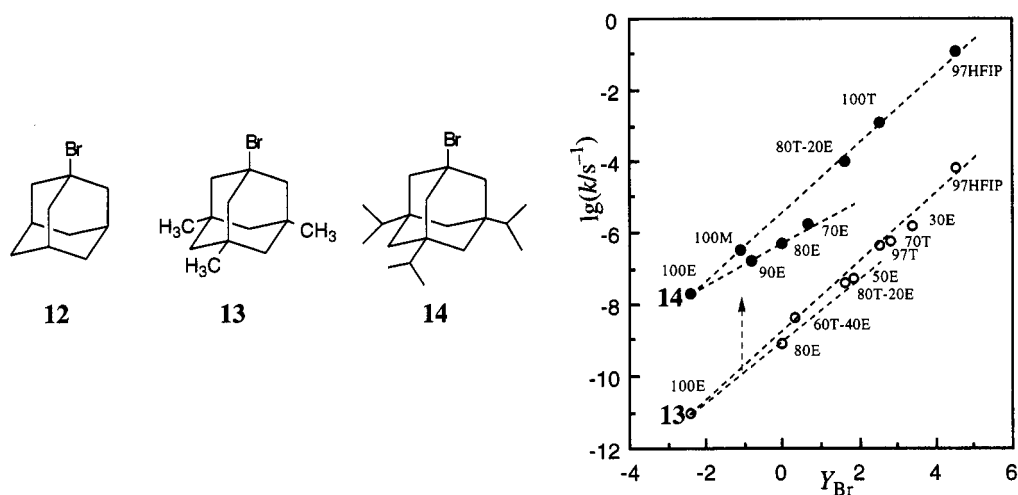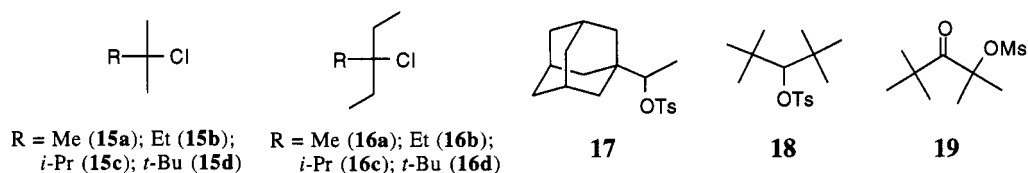


12     13     14



Fig. 8. Plots of lg $k$ values against $Y_{Br}$ for solvolyses of 13 and 14. The data points for 13 are shifted downward by 2 units for clarity. For the notation of solvents, see Figs. 1 and 2. $m$: 0.98 for both 13 and 14 in nonaqueous solvents.

## CONCLUDING REMARKS

Recently, Liu and co-workers compared the Grunwald–Winstein type relations between two series of tertiary alkyl chlorides, $RMe_2CCl$ (15) and $REt_2CCl$ (16), with R being changed as Me, Et, i-Pr, and t-Bu (21). They found excellent linear relations for 16c and 16d on the basis of Eq. 1 by using the $Y_{Cl}$ scale, but did not observe curvatures for aqueous ethanol solvents. Crowded secondary alkyl compounds, 17 and 18, were found to solvolyze without appreciable nucleophilic solvent participation (22–24), and decrease in *cationic solvation* associated with neighboring group participation was proposed.



R = Me (15a); Et (15b);      R = Me (16a); Et (16b);          17          18          19
i-Pr (15c); t-Bu (15d)       i-Pr (16c); t-Bu (16d)

Undoubtedly, 1-adamantyl and *tert*-butyl groups directly attached to the reaction center are good backside-shielding substituents. However, they have the disadvantage to cause σ-assisted ionization of secondary substrates. (1-Adamantyl)methyl and neopentyl substituents not only preclude σ-assisted ionization, but

also effectively shield the backside of the carbenium carbon. It has also been shown that a pivaloyl (*t*-BuCO) group in **19** also efficiently inhibits the nucleophilic solvent participation in solvolysis (25).

Experimental distinction between *nucleophilic solvent participation, cation solvation,* and *hydrophobic solvation* in solvolytic reactions may not be easily accomplished. However, systematic studies by controlling steric circumstances around the cationic center with remote substituents, such as a *tert*-butyl or a 1-adamantyl group in **6–11** and isopropyl groups in **14**, are expected to shed light on the details of solvent interaction in solvolytic reactions. Theoretical calculations on solvation models, determinations of gas-phase stabilities of carbocations, and information on cluster structures in aqueous organic solvents will greatly facilitate the progress of this field.

## ACKNOWLEDGMENTS

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