Influence of Alkyl Substitution on the Gas-Phase Stability of 1-Adamantyl Cation and on the Solvent Effects in the Solvolysis of **1-Bromoadamantane**

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1-Adamantyl cations having three methyl groups or one, two, or three isopropyl groups on the 3-, 5-, and 7-positions were found by FT ICR to be more stable than the 1-adamantyl cation and that the stability increases with the number of isopropyl group. The relative stabilities calculated by PM3 were in good agreement with the experimental results. In contrast, the sequence of the rates for the solvolysis in nonaqueous solvents are $3,5,7-(Me)_3-1-AdBr < 1$ -bromoadamantane (1-AdBr) $< 3,5,7-(n-Pr)_3-1-AdBr < 3,5,7-(i-Pr)_3-1-AdBr$. The rates of solvolysis of $3,5,7-(i-Pr)_3-1-AdBr$ and 3,5,7-(n-Pr)₃-1-AdBr relative to 1-AdBr at 25 °C are 15 and 3.8 in EtOH, respectively, but markedly decreases with the increase in the amount of added water, reaching 0.84 and 0.15, respectively, in 60% EtOH. Reflecting these effects of water, the Grunwald-Winstein (GW) relationship for 3,5,7- $(i-Pr)_3$ -1-AdBr and 3,5,7- $(n-Pr)_3$ -1-AdBr against Y_{Br} is linear for nonaqueous alcohols (EtOH, MeOH, TFE-EtOH, TFE, 97% HFIP), but marked downward deviations are observed for aqueous organic solvents, in particular, aqueous ethanol and aqueous acetone. The effect of the alkyl substituents to diminish relative solvolytic reactivity in EtOH-H₂O mixtures may be ascribed to a blend of steric hindrance to Br ϕ nsted base-type hydration to the β -hydrogens and hydrophobic interaction of the alkyl groups with ethanol to make the primary solvation shell less ionizing. The introduction of one nonyl group to the 3-position showed much smaller deviations in the GW relationship than the case of 3,5,7-(n-Pr)₃-1-AdBr. The markedly decelerated solvolysis of alkylated 1-bromoadamantanes in aqueous organic solvents is a kinetic version of anomalously diminished dissociation of alkylbenzoic acids in aqueous ethanol and aqueous tert-butyl alcohol that was demonstrated by Wepster and co-workers a decade ago and ascribed to hydrophobic effects.

Introduction

Substituent effects on the rates of solvolysis of bridgehead compounds and on the stability of bridgehead carbocations have been a long-standing subject in physical organic chemistry. The bridgehead systems that have been actively studied are 1-adamantyl,^{1a-h} 1-bicyclo[2.2.2]octyl, 1a,i 1-bicyclo[1.1.1]pentyl, 2a-d 1-bicyclo[2.2.1]heptyl, 2e,f and cubyl³ systems. In particular, the 1-adamantyl system containing a substituent on one of the other three equivalent bridgehead positions has been subjected to extensive studies because of the wide availability of substrates. Among various substituents, simple alkyl groups sometimes show peculiar behavior. Schleyer and co-workers found that the order of solvolysis rates is Me < H \sim Et < *i*-Pr < *t*-Bu for 3-alkyl-1-bromoadamantanes^{1b} and Me \leq Et \leq *i*-Pr \leq *t*-Bu \leq H for 4-alkyl-1-bicyclo-[2.2.2]octyl brosylates.^{1b} Grob and co-workers^{1c} and Perkins et al.^{1f} carried out similar studies. The variable behavior of hydrogen has been ascribed to differential solvation,^{1c} steric effects of the alkyl groups on molecular geometry,1b,f and possible electron-withdrawing effect1a of a methyl substituent. Introduction of three methyl groups to the 3-, 5-, and 7-positions of 1-bromoadaman-

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Gas- and Liquid-Phase Stability of 1-Adamantyl Cations

 $X = H, OH, Br, CO_2H, COCI$

tane (1Br) decelerates the solvolysis rate by a factor of $3.^{1a,c}$ Meanwhile, the three methyl groups in the 3,5,7trimethyl-1-adamantyl cation (2⁺) causes upfield shift of the bridgehead cationic carbon of 1⁺ by 5.9 ppm, from δ 300 to 294.1, showing that the methyl substituents actually behave as electron-donating groups.⁴ Calculations (STO-3G) indicate that the methyl group on the 3-position stabilizes the 1-adamantyl cation by 1.23 kcal mol⁻¹.^{1j} To our knowledge, the above anomalous effect of the alkyl substituents on solvolytic reactivity has not been clarified. We wished first to obtain unambiguous evidence for the effect of alkyl substituents on the stability of 1-adamantyl cation by the Fourier Transform Ion Cyclotron Resonance Spectroscopy (FT ICR) technique and theoretical calculations.

The second objective was to examine how the size of the alkyl substituents affect the Grunwald-Winstein⁵ (GW) relationship. Recently, one of us (K.T.) reported that highly crowded tertiary alkyl chlorides show downward dispersions of aqueous ethanol data points in the GW relationship.⁶ As a possible cause, steric hindrance to the Br ϕ nsted base-type solvation of water to β -hydrogens⁷ was proposed.^{6a} Meanwhile, two different explanations were suggested. Bentley's interpretation was related to possible mechanistic change to one-step olefin forming reaction.^{8a} Actually, the major product was a mixture of olefins (without skeletal rearrangement). The other comment by Kevill included possible reduced ion pair return.^{8b} Although the extent of ion-pair return was unknown, the major formation of olefins led Kevill to an interpretation that the fast deprotonation from ion pair by the chloride ion would be much faster than its nucleophilic attack toward the cationic carbon.^{8b} Consequently, we decided to examine the GW relationship in the solvolysis of 1-bromoadamantanes having alkyl substituents on the 3-, 5-, and 7-positions, which never give olefinic products, and the extent of ion pair return was thought not to be



^a Key: (a) 2 CH₃MgI; (b) TFA then aq Na₂CO₃; (c) HCO₂H/H₂SO₄/CCI₄; (d) SOCl₂.

much different from that of 1-bromoadamantane that is the standard compound for the $Y_{\rm Br}$ scale⁹ of the GW relationship.

Results

1. Synthesis. Among the eight alkylated 1-bromoadamantanes used in this work, the 3,5,7-trimethyl,^{1a,c,f} 3-isopropyl,^{1b,c} and 3-propyl¹⁰ derivatives (**2**Br, **3a**Br, and **4a**Br, respectively) had been reported. In the present work, **3a**Br, **4a**Br, and the other new bromides were prepared by the following routes.

1.1. 3-Isopropyl-, 3,5-Diisopropyl-, and 3,5,7-Triisopropyl-1-bromoadamantanes (**3a**Br, **3b**Br, and **3c**Br). The synthesis of **3a**OH and **3b**OH starting from 1-adamantanecarboxylic acid was reported by Kovalev et al.¹¹ We converted **3b**OH to the corresponding carboxylic acid, which was then subjected to the process that had been employed for the synthesis of **3b**OH to give **3c**OH (Scheme 1). The three alcohols were converted to the corresponding bromides with PBr₃.

1.2. 3-Propyl-, 3,5-Dipropyl-, 3,5,7-Tripropyl-, and 3-Nonyl-1-bromoadamantanes (4aBr, **4b**Br, **4c**Br, and **5**Br). An efficient alkylation method of 1-bromoadamantane with alkyl Grignard reagents was reported by Eguchi et al.,¹² which was used here to synthesize 1-propyl-, 1,3-dipropyl-, and 1,3,5-tripropyl-adamantanes (**4a**H, **4b**H, and **4c**H) (Scheme 2). 1-Nonyladamantane (**5**H) was prepared similarly. These were converted to **4a**Br, **4b**Br, **4c**Br, and **5**Br by direct bromination with Br₂.

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^a Key: (a) PrMgBr/CH₂Cl₂; (b) Br₂/CCl₄.

2. ICR Experiments. The experiments were performed on a modified Bruker CMS-47 Fourier Transform ICR mass spectrometer^{13a} used in previous studies.^{13b,14} The substantial field strength of its superconducting magnet (4.7 T) easily allows the storage and study of ions for periods of 20-30 s. The experimental method is based on the classical gas-phase bromide exchange^{15,16} between two different carbocations, reaction 1:

$$R_1^+(g) + R_2Br(g) \rightleftharpoons R_2^+(g) + R_1Br(g) [K_p, \Delta G^{\circ}(1) (1)]$$

The standard Gibbs energy change for reaction 1, $\Delta G^{\circ}(1)$, was obtained through eq 2:

$$\Delta G^{\circ}(1) = -RT \ln K_{\rm p} \tag{2}$$

The partial pressures of the neutral reagents, as determined by a Bayard–Alpert gauge, were corrected according to Bartmess and Georgiadis¹⁷ using the average molecular polarizabilities, $\alpha(ahc)$ calculated according to Miller.¹⁸ Uncertainties on the $\Delta G^{\circ}(1)$ values are estimated at 0.4 kcal mol⁻¹. A significant part of this uncertainty originates in the adsorption of these compounds onto the inner surface of the vacuum system. The direct comparison of 2^+ and $3a^+$ could not be carried out because they are isomeric species. The experimental results are summarized in Figure 1.

The results in Figure 1 can be used to obtain experimental, averaged values of $\Delta G^{\circ}(3)$.

$$\mathbf{1}\mathrm{Br}(\mathbf{g}) + \mathbf{R}^+(\mathbf{g}) \rightleftharpoons \mathbf{1}^+(\mathbf{g}) + \mathbf{R}\mathrm{Br}(\mathbf{g}) \left[\Delta G^{\circ}(3) - (3)\right]$$





Figure 1. Summary of the experimental standard Gibbs energy for reaction 1 obtained by FT ICR at experimental uncertainty ± 0.4 kcal mol⁻¹. The stability of the ions increases downward. All values in kcal mol⁻¹.

Table 1. Experimental Standard Gibbs Energy Changes
of Reaction 3, $\Delta G^{\circ}(3)^{a}$

cation	$\Delta G^{\circ}(3)/\text{kcal mol}^{-1}$	
1+	$(0.0)^{b}$	
2 +	-2.2^{c}	
$3a^+$	-2.2^{c}	
$3b^+$	-3.8^{c}	
$3c^+$	-5.6^{c}	

^{*a*} All values in kcal mol⁻¹. ^{*b*} Reference value. ^{*c*} Estimated uncertainty, ± 0.4 kcal mol⁻¹.

Table 2. Gas-Phase Stabilities of Alkyl Substituted
1-Adamantyl Cations Relative to $1^+[\Delta H^{\circ}(3, \text{theor})]$
Calculated by PM3

	$\Delta H^{\circ}(3, \text{theor})/\text{kcal mol}^{-1}$			
substituent (R)	3-(R)	3,5-(R) ₂	3,5,7-(R) ₃	
Н	(0.0) ^a	(0.0) ^a	(0.0) ^a	
Me	-0.76	-1.47	-2.13	
Et	-1.43	-2.76	-4.07	
<i>i</i> -Pr	-2.07	-3.95	-5.68	
<i>n</i> -Pr	-1.65	-3.48	$(-5.0 \pm 0.1)^{b}$	
<i>t</i> -Bu	-2.86	-5.34	-7.64	

 a Reference value. b Estimated from a plot of $\Delta H^o(3, theor)$ against the number of the substituent. See Figure S1 in Supporting Information.

 $\Delta G^{\circ}(3)$ is a quantitative measure of the relative thermodynamic stabilities of the carbocations with respect to 1-adamantyl cation (1⁺) in the gas phase. The $\Delta G^{\circ}(3)$ values are presented in Table 1.

3. PM3 Calculations. PM3 calculations were carried out on the heat of exchange reaction for eq 3 $[\Delta H^{\circ}(3, \text{theor})]$ for mono-, di-, and trisubstituted 1-adamantyl cations having Me, Et, i-Pr, n-Pr, or t-Bu substituents through the MOPAC system.¹⁹ The most stable conformers were sought; however, because of too many conformations of $4c^+$ and 4cBr, the energy of $4c^+$ was obtained not by calculations, but by estimation as -5.0 \pm 0.1 kcal mol^{-1} by comparing a plot of $\Delta H^{\circ}(3, theor)$ against the number of the *n*-Pr group with those for the other substituents (see Supporting Information). All the calculated results are summarized in Table 2. Calculations on $3a^+$, $3b^+$, and $3c^+$ by AM1 gave energies about 14% larger than the values in Table 2. Comparisons with the FT ICR data in Table 1 reveal that PM3 calculations show very good agreement.

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 Table 3. Rate Constants of Solvolysis of 1-Bromo-3,5,7-trialkyladamantanes and Rate Ratios to 1-Bromoadamantane (1Br) at 25.0 °C^a

	k^{c}/\mathbf{s}^{-1}				rate rel to 1 Br		
$solvent^b$	3,5,7-(Me) ₃ (2 Br)	3,5,7-(<i>i</i> -Pr) ₃ (3c Br)	3,5,7-(<i>n</i> -Pr) ₃ (4c Br)	1-AdBr (1Br)	2 Br/ 1 Br	3c Br/ 1 Br	4cBr/1Br
100E	$9.7 imes10^{-10}$ d	$2.0 imes10^{-8}$ d,f	$4.9 imes10^{-9}$ d,g	$1.3 imes 10^{-9}$ h	0.75	15	3.8
90E-10W		$1.6 imes 10^{-7}$ d,i		$4 imes 10^{-8j}$		4.0	
80E-20W	$8.0 imes10^{-8}$ d,k	$5.3 imes10^{-7}$ d,l	$1.37 imes10^{-7}$ d,m	$2.8 imes10^{-7}{}^{j}$	0.29	1.9	0.49
70E-30W	$7.8 imes10^{-7}$ d,n	$1.73 imes 10^{-6}$ o,p	$3.94 imes10^{-7}{}^o$	$1.33 imes 10^{-6j}$	0.59	1.1	0.30
60E-40W		$4.29 imes10^{-6}$ o	$7.72 imes10^{-7~o}$	$5.1 imes10^{-6}{}^{j}$		0.84	0.15
50E-50W	$5.49 imes10^{-6}$ o, q			$2.12 imes 10^{-5j}$	0.26		
30E-70W	$1.57 imes 10^{-4}$ d,r			$6.98 imes10^{-4}{}^{j}$	0.22		
100M	$2.0 imes10^{-8}$ d,r,s	$3.40 imes10^{-7}$ d,t	$8.6 imes10^{-8}$ d,u	$2.1 imes 10^{-8j}$	0.95	16	4.1
90M-10W		$1.63 imes 10^{-6}$ o,r		$2.0 imes10^{-7}{}^{j}$		8.2	
80M-20W	$7.8 imes10^{-7}$ d,v	$7.31 imes10^{-6}$ o,r	$2.39 imes10^{-6}$ o,r	$1.40 imes10^{-6}{}^{j}$	0.56	5.2	1.7
70M-30W		$2.83 imes10^{-5~o}$		$7.3 imes10^{-6j}$		3.9	
60M-40W		$1.01 imes 10^{-4}$ o,r	$3.11 imes 10^{-5~o,r}$	$3.1 imes 10^{-5j}$		3.3	1.0
100T		$1.24 imes 10^{-3}{}^q$	$2.98 imes10^{-4}{}^o$	$9.22 imes10^{-5}$ $^{\scriptscriptstyle W}$		14	3.2
97T	$4.59 imes10^{-5}$ o			$9.5 imes10^{-5j}$	0.50		
70T-30W	$5.60 imes10^{-5}$ o	$9.51 imes 10^{-4}$ o,r	$2.66 imes10^{-4}$ o,r	$1.71 imes10^{-4}$ $^{\scriptscriptstyle W}$	0.33	5.6	1.6
50T-50W		$9.81 imes 10^{-4}$ o,r		$3.10 imes10^{-4}$ $^{\scriptscriptstyle W}$		3.2	
80T-20E	$3.90 imes10^{-6}$ o	$1.03 imes10^{-4}{}^o$	$2.91 imes10^{-5~o}$	$7.32 imes10^{-6}$ $^{\scriptscriptstyle W}$	0.53	14	4.0
60T-40E	$4.28 imes 10^{-7}$ d,x	$8.82 imes10^{-6}{}^o$	$1.48 imes10^{-6}{}^o$	$7.64 imes10^{-7}$ $^{\scriptscriptstyle W}$	0.56	12	1.9
97HFIP-3W	$7.02 imes 10^{-3~q,r}$	$1.31 imes 10^{-1}$ $_{q,r}$	$4.19 imes10^{-2}$ q,r	$9.1 imes 10^{-3j}$	0.77	14	4.6
80A-20W		$1.10 imes 10^{-7}$ d,y		$6 imes 10^{-8j}$		1.8	
70A-30W		$5.16 imes10^{-7}$ d,z	$1.48 imes10^{-7}$ d,aa	$5 imes 10^{-7j}$		1.0	0.3

^a Solvolysis was generally conducted in the presence of 25% excess of 2,6-lutidine for titrimetric runs and $(2\sim10) \times 10^{-4}$ mol L⁻¹ 2,6-lutidine for conductometric runs. ^b E, M, A, T, and W denote ethanol, methanol, acetone, 2,2,2-trifluoroethanol, and water, respectively, and the preceding figures denote vol % of each component at 25 °C except for T-W and 97HFIP systems, which are expressed by wt %. ^c Most of the data were obtained from duplicate runs within experimental errors of $\pm 2\%$ and $\pm 0.5\%$ in titrimetric and conductometric measurements, respectively. ^{*d*} Extrapolated from data at higher temperatures. ^{*e*} k: $9.51 \times 10^{-7} \text{ s}^{-1}$ (75.0 °C); $1.49 \times 10^{-5} \text{ s}^{-1}$ (100.0 °C); $\Delta H^{\ddagger} = 27.8 \text{ kcal mol}^{-1}; \Delta S^{\ddagger} = -6.5 \text{ cal mol}^{-1}\text{K}^{-1}. {}^{f}k: 1.19 \times 10^{-5} \text{ s}^{-1} (75.0 \text{ °C}); 1.53 \times 10^{-4} \text{ s}^{-1} (100.0 \text{ °C}); \Delta H^{\ddagger} = 25.8 \text{ kcal mol}^{-1}; \Delta S^{\ddagger} = -7.2 \text{ cal mol}^{-1}\text{K}^{-1}. {}^{g}k: 2.98 \times 10^{-6} \text{ s}^{-1} (75.0 \text{ °C}); 3.86 \times 10^{-5} \text{ s}^{-1} (100.0 \text{ °C}); \Delta H^{\ddagger} = 25.8 \text{ kcal mol}^{-1}; \Delta S^{\ddagger} = -9.9 \text{ cal mol}^{-1}\text{K}^{-1}. {}^{h}\text{ For}$ estimation of this value, see text. Bentley estimated a value 1×10^{-9} s⁻¹ (ref 9a). ^{*i*} *k*: 7.38 × 10⁻⁵ s⁻¹ (75.0 °C); 8.47 × 10⁻⁴ s⁻¹ (100.0 °C); $\Delta H^{\sharp} = 24.6 \text{ kcal mol}^{-1}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{K}^{-1}. \text{ / Ref 9a. } ^{k} k: 2.39 \times 10^{-6} \text{ s}^{-1} (50.0 \text{ °C}); \\ 4.40 \times 10^{-5} \text{ s}^{-1} (75.0 \text{ °C}); \\ \Delta H^{\sharp} = 25.5 \text{ kcal mol}^{-1}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{K}^{-1}. \text{ / Ref 9a. } ^{k} k: 2.39 \times 10^{-6} \text{ s}^{-1} (50.0 \text{ °C}); \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{K}^{-1}. \text{ / Ref 9a. } ^{k} k: 2.39 \times 10^{-6} \text{ s}^{-1} (50.0 \text{ °C}); \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{K}^{-1}. \text{ / Ref 9a. } ^{k} k: 2.39 \times 10^{-6} \text{ s}^{-1} (50.0 \text{ °C}); \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{K}^{-1}. \text{ / Ref 9a. } ^{k} k: 2.39 \times 10^{-6} \text{ s}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7.0 \text{ cal mol}^{-1} \text{ (50.0 °C)}; \\ \Delta S^{\sharp} = -7$ $\Delta S^{\ddagger} = -5.6$ cal mol⁻¹K⁻¹. A reported value at 75.0 °C is 6.93×10^{-5} s⁻¹ (ref 1c). ¹k: 1.55×10^{-5} s⁻¹ (50.0 °C); 2.78×10^{-4} s⁻¹ (75.0 °C); $\Delta H^{\ddagger} = 25.2 \text{ kcal mol}^{-1}; \Delta S^{\ddagger} = -2.6 \text{ cal mol}^{-1} \text{K}^{-1}. \ {}^{m} \text{k}; \ 4.31 \times 10^{-6} \text{ s}^{-1} (50.0 \text{ °C}); 8.22 \times 10^{-5} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\ddagger} = 25.8 \text{ kcal mol}^{-1}; \Delta S^{\ddagger} = -2.6 \text{ cal mol}^{-1} \text{K}^{-1}. \ {}^{m} \text{k}; \ 4.31 \times 10^{-6} \text{ s}^{-1} (50.0 \text{ °C}); 8.22 \times 10^{-5} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\ddagger} = 25.8 \text{ kcal mol}^{-1}; \Delta S^{\ddagger} = -2.6 \text{ cal mol}^{-1} \text{K}^{-1}. \ {}^{m} \text{k}; \ 4.31 \times 10^{-6} \text{ s}^{-1} (50.0 \text{ °C}); 8.22 \times 10^{-5} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\ddagger} = 25.8 \text{ kcal mol}^{-1}; \Delta S^{\ddagger} = -2.6 \text{ cal mol}^{-1} \text{K}^{-1} \text{K}^{-1}$ -3.4 cal mol⁻¹K⁻¹. n k: 1.74×10^{-5} s⁻¹ (50.0 °C); 2.48×10^{-4} s⁻¹ (75.0 °C); $\Delta H^{\ddagger} = 24.8$ kcal mol⁻¹; $\Delta S^{\ddagger} = -5.2$ cal mol⁻¹K⁻¹. o Determined titrimetrically. p The specific rate in the absence of 2,6-lutidine was 1.76×10^{-6} s⁻¹. q Extrapolated from data determined conductometrically in the absence of 2,6-lutidine. k: $9.83 \times 10^{-4} \text{ s}^{-1}$ (40.0 °C); $3.03 \times 10^{-3} \text{ s}^{-1}$ (50.0 °C); $\Delta H^{\ddagger} = 22.1 \text{ kcal mol}^{-1}$; $\Delta S^{\ddagger} = -1.8 \text{ cal mol}^{-1} \text{K}^{-1}$. r In the absence of 2,6-lutidine. s k: $5.78 \times 10^{-7} \text{ s}^{-1}$ (50.0 °C); $1.04 \times 10^{-5} \text{ s}^{-1}$ (75.0 °C); $\Delta H^{\ddagger} = 25.2 \text{ kcal mol}^{-1}$; $\Delta S^{\ddagger} = -9.0 \text{ cal mol}^{-1} \text{K}^{-1}$. t k: $1.01 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 1.83 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\sharp} = 25.3 \text{ kcal mol}^{-1} \text{ K}^{-1} \Delta S^{\sharp} = -3.1 \text{ cal mol}^{-1} \text{ K}^{-1} \cdot u \text{ k}; 4.21 \times 10^{-5} \text{ s}^{-1} (75.0 \text{ °C}); 5.02 \times 10^{-4} \text{ s}^{-1} (100.0 \text{ °C}); \Delta H^{\sharp} = 25.0 \text{ kcal mol}^{-1}; \Delta S^{\sharp} = -7.1 \text{ cal mol}^{-1} \text{ K}^{-1} \cdot u \text{ k}; 1.74 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 2.48 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\sharp} = 25.0 \text{ kcal mol}^{-1}; \Delta S^{\sharp} = -7.1 \text{ cal mol}^{-1} \text{ K}^{-1} \cdot u \text{ k}; 1.74 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 2.48 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\sharp} = 25.0 \text{ kcal mol}^{-1}; \Delta S^{\sharp} = -7.1 \text{ cal mol}^{-1} \text{ K}^{-1} \cdot u \text{ k}; 1.74 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 2.48 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\sharp} = 25.0 \text{ kcal mol}^{-1}; \Delta S^{\sharp} = -7.1 \text{ cal mol}^{-1} \text{ K}^{-1} \cdot u \text{ k}; 1.74 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 2.48 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\sharp} = 25.0 \text{ kcal mol}^{-1}; \Delta S^{\sharp} = -7.1 \text{ cal mol}^{-1} \text{ K}^{-1} \cdot u \text{ k}; 1.74 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 2.48 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\sharp} = 25.0 \text{ kcal mol}^{-1}; \Delta S^{\sharp} = -7.1 \text{ cal mol}^{-1} \text{ K}^{-1} \cdot u \text{ k}; 1.74 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 2.48 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\sharp} = 25.0 \text{ kcal mol}^{-1}; \Delta S^{\sharp} = -7.1 \text{ cal mol}^{-1} \text{ K}^{-1} \cdot u \text{ k}; 1.74 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 2.48 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\sharp} = 25.0 \text{ kcal mol}^{-1}; \Delta S^{\sharp} = -7.1 \text{ cal mol}^{-1} \text{ k}; 1.74 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 2.48 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\sharp} = 25.0 \text{ kcal mol}^{-1}; \Delta S^{\sharp} = -7.1 \text{ cal mol}^{-1} \text{ k}; 1.54 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 2.48 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\sharp} = 25.0 \text{ kcal mol}^{-1}; \Delta S^{\dagger} = -7.1 \text{ cal mol}^{-1} \text{ s}^{-1} \text{ cal mol}^{-1} \text{ s}^{-1} \text{ cal mol}^{-1} \text{ cal$ 23.1 kcal mol⁻¹; $\Delta S^{\ddagger} = -8.8$ cal mol⁻¹K⁻¹. "Reference 9c. "k: 8.85×10^{-6} s⁻¹ (50.0 °C); 1.18×10^{-4} s⁻¹ (75.0 °C); $\Delta H^{\ddagger} = 22.6$ kcal mol⁻¹; $\Delta S^{\ddagger} = -11.8 \text{ cal mol}^{-1} \text{K}^{-1}. \ \text{$'$ k$} \cdot 4.98 \times 10^{-5} \text{ s^{-1}} (75.0 \text{ }^{\circ}\text{C}); 5.72 \times 10^{-4} \text{ s^{-1}} (100.0 \text{ }^{\circ}\text{C}); \Delta H^{\ddagger} = 24.6 \text{ kcal mol}^{-1}; \Delta S^{\ddagger} = -7.8 \text{ cal mol}^{-1} \text{K}^{-1}. \ \text{$'$ k$} \cdot 10^{-5} \text{ s^{-1}} (75.0 \text{ }^{\circ}\text{C}); 5.72 \times 10^{-4} \text{ s^{-1}} (100.0 \text{ }^{\circ}\text{C}); \Delta H^{\ddagger} = 24.6 \text{ kcal mol}^{-1}; \Delta S^{\ddagger} = -7.8 \text{ cal mol}^{-1} \text{K}^{-1}. \ \text{s^{-1}} = -7.8 \text{ cal mol}^{-1} \text{s^{-1}} = -7.8 \text{$ $1.56 \times 10^{-5} \text{ s}^{-1} (50.0 \text{ °C}); 2.89 \times 10^{-4} \text{ s}^{-1} (75.0 \text{ °C}); \Delta H^{\ddagger} = 25.5 \text{ kcal mol}^{-1}; \Delta S^{\ddagger} = -1.7 \text{ cal mol}^{-1} \text{K}^{-1}.$ × 10⁻⁵ s⁻¹ (75.0 °C); $\Delta H^{\ddagger} = 25.0$ kcal mol⁻¹; $\Delta S^{\ddagger} = -5.8$ cal mol⁻¹K⁻¹.

Table 4.	Rate Constants of Solvolysis of 1-Bromo-3,5-dialkyladamantanes and Rate Ratios to 1-Bromoadamantane (1)	Br)
	at 25.0 °C ^a	

			rate rel to $1\mathbf{Br}^d$	
solvent ^b	3,5-(<i>i</i> -Pr) ₂ (3b Br)	3,5-(<i>n</i> -Pr) ₂ (4b Br)	3b Br/ 1 Br	4b Br/ 1 Br
100E	$8.3 imes10^{-9}$ e,f	$4.0 imes10^{-9}$ e,g	6.4	3.1
80E-20W	$8.10 imes10^{-7~e,h}$	$1.9 imes 10^{-7}$ e,i	2.9	0.68
70E-30W	$2.26 imes10^{-6}$	$5.40 imes10^{-7}$	1.7	0.41
80M-20W	$6.41 imes10^{-6}$	$1.84 imes10^{-6}$	4.6	1.3
60T-40E	$4.12 imes10^{-6}$	$1.34 imes 10^{-6}$	5.4	1.8
80T-20E	$3.76 imes10^{-5}$	$1.38 imes10^{-5}$	5.1	1.9

^{*a*} Solvolysis was conducted titrimetrically in the presence of 25% excess of 2,6-lutidine ^{*b*} E, M, T, and W denote ethanol, methanol, 2,2,2-trifluoroethanol, and water, respectively, and the preceding figures denote vol % of each component at 25 °C. ^{*c*} Most of the data were obtained from duplicate runs within experimental error of $\pm 2\%$. ^{*d*} For the specific rates of **1**Br, see Table 1. ^{*e*} Extrapolated from data at higher temperatures. ^{*f*} *k*: 9.22 × 10⁻⁶ s⁻¹ (75.0 °C); 1.52 × 10⁻⁴ s⁻¹ (100.0 °C); $\Delta H^{\ddagger} = 28.5$ kcal mol⁻¹; $\Delta S^{\ddagger} = -0.4$ cal mol⁻¹K⁻¹. ^{*f*} *k*: 1.58 × 10⁻⁷ s⁻¹ (50.0 °C); 3.68 × 10⁻⁶ s⁻¹ (75.0 °C); $\Delta H^{\ddagger} = 27.5$ kcal mol⁻¹; $\Delta S^{\ddagger} = -4.5$ cal mol⁻¹K⁻¹. ^{*h*} *k*: 1.77 × 10⁻⁵ s⁻¹ (50.0 °C); 2.47 × 10⁻⁴ s⁻¹ (75.0 °C); $\Delta H^{\ddagger} = 23.1$ kcal mol⁻¹; $\Delta S^{\ddagger} = -9.3$ cal mol⁻¹K⁻¹. ^{*i*} *k*: 5.58 × 10⁻⁶ s⁻¹ (50.0 °C); 1.01 × 10⁻⁴ s⁻¹ (75.0 °C); $\Delta H^{\ddagger} = 25.3$ kcal mol⁻¹; $\Delta S^{\ddagger} = -4.4$ cal mol⁻¹K⁻¹.

4. Solvolysis Studies

4.1. Rate Studies. The rates of solvolysis were determined titrimetrically or conductometrically. Generally, the solvolysis was conducted in the presence of 25% excess of 2,6-lutidine, but some rate runs in several aqueous solvents were conducted in its absence, since the titrimetric end-point became obscured or conductometric measurements became difficult. The rates that are too

slow for direct measurements at 25 °C were obtained by extrapolation from data at higher temperatures. The rate constants at 25.0 °C are summarized in Tables 3–5. The rate of **1**Br in EtOH at 25.0 °C had been roughly estimated by Bentley and Carter to be $1 \times 10^{-9} \text{ s}^{-1.9a}$ We found that a logarithmic plot of the rate constants for **3**cBr against those for **1**Br for the solvolysis in nonaqueous solvents, 97% HFIP, 100% TFE, 80% TFE–20%

 Table 5. Rate Constants of Solvolysis of 1-Bromo-3-alkyladamantanes and Rate Ratios to 1-Bromoadamantane (1Br) at 25.0 °C a

		k^{c}/s^{-1}			rate rel to $1\mathbf{B}\mathbf{r}^d$	
$solvent^b$	3- <i>i</i> -Pr (3a Br)	3- <i>n</i> -Pr (4a Br)	3- <i>n</i> -C ₉ H ₁₉ (5 Br)	3a Br/ 1 Br	4a Br/ 1 Br	5 Br/ 1 Br
100E	$3.5 imes10^{-9}$ e,f	$2.1 imes 10^{-9}$ e,g	$2.2 imes 10^{-9}$ e,h	2.7	1.6	1.7
80E-20W	$5.4 imes10^{-7}$ e,i	$2.6 imes 10^{-7}$ e.j	$2.1 imes 10^{-7}$ e,k	1.9	0.93	0.75
70E-30W	$2.87 imes10^{-6}$	$1.19 imes10^{-6}$	$8.17 imes10^{-7}$	2.2	0.89	0.61
80M-20W	$3.44 imes10^{-6}$	$2.24 imes10^{-6}$	$1.40 imes10^{-6}$	2.5	1.6	1.0
60T-40E	$1.93 imes10^{-6}$	$1.08 imes10^{-6}$	$8.85 imes10^{-7}$	2.5	1.4	1.2
80T-20E	$1.93 imes10^{-5}$	$1.01 imes 10^{-5}$	$8.39 imes10^{-6}$	2.6	1.4	1.1

^{*a*} Solvolysis was conducted titrimetrically in the presence of 25% excess of 2,6-lutidine. ^{*b*} E, M, T, and W denote ethanol, methanol, 2,2,2-trifluoroethanol, and water, respectively, and the preceding figures denote vol % of each component at 25 °C. ^{*c*} Most of the data were obtained from duplicate runs within experimental error of $\pm 2\%$. ^{*d*} For the specific rates of **1**Br, see Table 1. ^{*e*} Extrapolated from data at higher temperatures. ^{*i*} *k*: 1.57 × 10⁻⁷ s⁻¹ (50.0 °C); 4.08 × 10⁻⁶ s⁻¹ (75.0 °C); $\Delta H^{\pm} = 28.5$ kcal mol⁻¹; $\Delta S^{\pm} = -1.5$ cal mol⁻¹K⁻¹. ^{*g*} *k*: 9.18 × 10⁻⁸ s⁻¹ (50.0 °C); 2.30 × 10⁻⁶ s⁻¹ (75.0 °C); $\Delta H^{\pm} = 28.1$ kcal mol⁻¹; $\Delta S^{\pm} = -3.6$ cal mol⁻¹K⁻¹. ^{*h*} *k*: 9.19 × 10⁻⁸ s⁻¹ (50.0 °C); 2.30 × 10⁻⁶ s⁻¹ (75.0 °C); $\Delta H^{\pm} = 28.1$ kcal mol⁻¹; $\Delta S^{\pm} = -3.6$ cal mol⁻¹K⁻¹. ^{*h*} *k*: 9.19 × 10⁻⁸ s⁻¹ (50.0 °C); 2.37 × 10⁻⁷ s⁻¹ (75.0 °C); $\Delta H^{\pm} = 28.1$ kcal mol⁻¹; $\Delta S^{\pm} = -3.6$ cal mol⁻¹K⁻¹. ^{*h*} *k*: 9.19 × 10⁻⁸ s⁻¹ (75.0 °C); $\Delta H^{\pm} = 28.0$ kcal mol⁻¹; $\Delta S^{\pm} = -4.2$ cal mol⁻¹K⁻¹. ^{*i*} *k*: 1.28 × 10⁻⁵ s⁻¹ (50.0 °C); 1.94 × 10⁻⁴ s⁻¹ (75.0 °C); $\Delta H^{\pm} = 23.7$ kcal mol⁻¹; $\Delta S^{\pm} = -7.8$ cal mol⁻¹K⁻¹. ^{*i*} *k*: 7.03 × 10⁻⁶ s⁻¹ (50.0 °C); 1.20 × 10⁻⁴ s⁻¹ (75.0 °C); $\Delta H^{\pm} = 24.7$ kcal mol⁻¹; $\Delta S^{\pm} = -5.6$ cal mol⁻¹K⁻¹. ^{*i*} *k*: 6.06 × 10⁻⁶ s⁻¹ (50.0 °C); 1.06 × 10⁻⁴ s⁻¹ (75.0 °C); $\Delta H^{\pm} = 25.0$ kcal mol⁻¹; $\Delta S^{\pm} = -5.2$ cal mol⁻¹K⁻¹.

EtOH, 60% TFE–40% EtOH, and MeOH, give a good straight line. Extrapolation to the EtOH data point for **3c**Br in this plot gave an estimated rate constant for **1**Br of $(1.3 \pm 0.1) \times 10^{-9} \text{ s}^{-1}$. The details are given in the Supporting Information.

4.2. Products of Solvolysis of 1Br and 3cBr in 80% **EtOH.** To examine if isopropyl substituents on the 3-, 5-, and 7-positions exert effects on the product partition (selectivity) in an ethanol-water mixture, the distribution of ethyl ether and alcohol products was determined for the solvolyis in 80% ethanol-20% water (v/v) in the presence of excess 2,6-lutidine at 25 and 75 °C.²⁰ The product distributions at 75 °C were determined at 10 half-lives, but those at 25 °C were analyzed at 1.5 or 2.9 half-lives. The ethyl ether/alcohol product ratios at 75 °C were 37 \pm 2/63 \pm 2 and 36 \pm 1/64 \pm 1 for 1Br and 4cBr, respectively. The corresponding product ratios at 25 °C were $38 \pm 1/62 \pm 1$ and $40 \pm 1/60 \pm 1$, respectively, which are similar to those at 75 °C. The product distributions from **1**Br afford selectivity ratios $k_{\rm E}/k_{\rm W}$ of 0.50 at 25 °C and 0.48 at 75 °C: reported values are 0.74 at 25 °C,^{21a} 0.53 at 75 °C,^{21b} and 0.48 at 100 °C.^{21c}

Discussion

1. Effects of Alkyl Substituents on Relative Stabilities of 1-Adamantyl Cations in Gas-Phase and in Solution. As previously estimated from STO-3G calculations on the 3-methyl-1-adamantyl cation,^{1j} the present FT ICR experiments reveal that the introduction of three methyl or one to three isopropyl substituents to the 3- (and 5-, 7-) position(s) stabilizes the 1-adamantyl cation (Table 1). As evident from a plot of limited numbers of experimental gas-phase stabilities $[\Delta G^{\circ}(3)]$ for eq 3 against the stabilities obtained by PM3 calculations $[\Delta H^{\circ}(3, \text{theor})]$ (Figure 2), the gas-phase substituent effect obtained by FT ICR is nearly additive within the experimental error ± 0.4 kcal mol⁻¹. Notwithstanding the experimental uncertainty, the first substituent appears most effective. From the data in Table 1, the differences in stability (kcal mol⁻¹) are 2.2 \pm 0.4 for **3a**⁺ vs **1**⁺, 1.6 \pm 0.4 for $3\mathbf{b}^+$ vs $3\mathbf{a}^+$, and 1.8 ± 0.4 for $3\mathbf{c}^+$ vs $3\mathbf{b}^+$. The



Figure 2. A plot of experimental $\Delta G^{\circ}(3)$ obtained by FT ICR against $\Delta H^{\circ}(3, \text{theor})$ calculated by PM3 for various 1-adamantyl cations. The energies are relative to 1^+ . Slope: 0.97; r. 0.999.

respective stability differences by PM3 calculation are 2.07, 1.88, and 1.73 kcal mol⁻¹.

2. Solvolysis Rate Ratios and Gas-Phase Stabilities of Carbocations. The solvolysis rate ratios between alkylated 1-bromoadamantanes and 1-bromoadamantane (1Br) are summarized in Tables 3–5. First, as previously reported for a few solvents, ^{1a,c} 1-bromo-3,5,7-trimethyladamantane (2Br) solvolyzes slower than 1Br in all the solvents examined (Table 3). Besides, it was revealed that the addition of water to ethanol, methanol, and TFE decreases the rate ratio of 2Br/1Br, although rigorous comparison may not be permitted since the rate data include extrapolation from data at higher temperatures. Thus, the rate ratio changes in the following manner; 0.75 (100% EtOH), 0.29 (80% EtOH), 0.59 (70% EtOH), 0.26 (50% EtOH), and 0.22 (30% EtOH); 0.95 (100% MeOH) and 0.56 (80% MeOH); 0.50 (97% TFE) and 0.33 (70% TFE).

The effect of water on the rate ratio is more marked when isopropyl or propyl substituents are introduced. For example, the rate ratio of 15 for **3c**Br/**1**Br in EtOH decreases with increase in water content in such a way to 4.0 (90% EtOH), 1.9 (80% EtOH), 1.1 (70% EtOH), and finally below unity, 0.84 (60% EtOH) (Table 3). A similar trend is also found in MeOH $-H_2O$ and TFE $-H_2O$. The **4c**Br/**1**Br rate ratio also shows a similar trend: it is noted

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Figure 3. A plot of logarithms of specific rates for the solvolysis of 1Br, **3a**Br, **3b**Br, and **3c**Br in various solvents against the number of isopropyl group: EtOH (\bullet); 60% TFE–40% EtOH (\blacksquare); 80% EtOH (\Box); 70% EtOH (\triangle).

that the rate ratio of 3.8 in EtOH decreases to 0.15 in 60% EtOH.

In the long history of solvolysis studies, "80% ethanol" has been used as a convenient solvent. In the Grunwald-Winstein relationship,⁵ 80% ethanol is used as the standard solvent. However, the data of the present study suggest that aqueous ethanol might result in a wrong conclusion regarding the stability of incipient carbocations and electron-donating ability of alkyl substituents. Representative situations are illustrated in Figure 3 by using the rate constants of Tables 3–5. The isopropylsubstituent effect on $\log k$ is essentially additive in nonaqueous solvents, such as 100% EtOH and 60% TFE-40% EtOH, whereas in 80% EtOH and 70% EtOH the introduction of the second or the third isopropyl substituent results in decreased solvolysis rates. This sort of anomaly is reflected in dispersion in the Grunwald-Winstein relationship. The probable causes are discussed in the following section.⁶ It is recommended that whenever the solvolytic reactivity is to be related with carbocation stability, the rates should be examined in nonaqueous solvents such as ethanol, methanol, TFE, TFE-EtOH, and 97% HFIP, and the use of aqueous mixtures should be avoided.

The Gibbs energies of activation relative to **1**Br in solvolysis $[\delta \Delta G^{\ddagger}_{solv}]$ can be obtained by eq 4, where k_0 and k are rate constants of **1**Br and other bromides in question, respectively.

$$\delta \Delta G^{\ddagger}_{\text{solv}} = -RT \ln(k/k_0) \tag{4}$$

The relation between $\delta\Delta G^{\dagger}_{solv}$ and gas-phase stability of carbocations [$\Delta G^{\circ}(3)$] has been one of central subjects in carbocation chemistry since the pioneering work by Schleyer and co-workers on the solvolytic reactivities of cage compounds.²² Figure 4 shows a plot of $-\delta\Delta G^{\dagger}_{solv}$ for 2Br, **3c**Br, and **4c**Br relative to **1**Br against PM3 calculated $\Delta H^{\circ}(3,$ theor) for the corresponding carbocations in Table 2. The solvents are EtOH, TFE, 80% TFE– 20% EtOH, 97% HFIP, and 80% EtOH. Notably, the data



Figure 4. A plot of $-\delta \Delta G^{\ddagger}$ (= $RT \ln(k_R/k_H)$) for the solvolysis of 3,5,7-trialkyl-1-bromoadamantanes in EtOH, TFE, 80% TFE–20% EtOH, 97% HFIP, and 80% EtOH at 25 °C against $-\Delta H^{\circ}$ (3,theor) of 3,5,7-trialkyl-1-adamantyl cations calculated by PM3. The energies are relative to those of the 1-adamantyl system: TFE (**I**); EtOH (**A**); 97% HFIP (**O**); 80% TFE–20% EtOH (\odot); 80% EtOH (\times).

points of each substrate for the first four nonaqueous solvents fall very close to each other to give a roughly linear correlation with a slope 0.5. In contrast, the points for 80% EtOH scatter below the correlation line.

The upward deviation of the data point for **1**Br by 1.4 kcal mol⁻¹ from the correlation line (Figure 4) suggests that **1**Br is subject to extra stabilization in the transition state of ionization, which is not evident in the 3,5,7-trialkyl systems. Br ϕ nsted base-type solvation toward relatively positive hydrogens on the 3-, 5-, and 7-positions²³ might be operative.

3. Grunwald–Winstein Relationship. In the revised Grunwald–Winstein (GW) equations $[\log(k/k_0) = mY_X]$ for solvolytic reactions of alkyl halides, the ionizing power (Y_X) of solvent is defined by $\log(k/k_0)$ for the solvolysis of 1-haloadamantanes, with m = 1 by definition. The k and k_0 are rate constants in a given solvent and 80% ethanol–20% water (v/v), respectively, at 25 °C, and X is a halogen leaving group. Many tertiary alkyl halides have been examined by the revised GW equations, and any dispersions in the $\log(k/k_0)$ vs Y_X plot ascribed to solvent effects other than polarity and electrophilic nature (toward the leaving group) of solvents, or possible mechanistic changes.

For example, nucleophilic solvent participation,^{5b,c} Br ϕ nsted base-type solvation to β -hydrogens,⁶ ion-pair return,^{8b} and concerted elimination^{8a} have been proposed as possible causes for various kinds of dispersion in the GW relations of simple and highly congested open-chain alkyl chlorides. In this respect, 3,5,7-trialkyl-1-bromoad-amantanes were thought as one of ideal candidates for

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⁽²³⁾ The ¹H NMR δ values for H(3) and H(2) of the 1-adamantyl cation are 5.19 and 4.19 ppm, respectively, indicating that H(3) is more positively charged than H(2) (ref 4).



Figure 5. A plot of log *k* values against Y_{Br} for the solvolysis of **2**Br (\blacksquare , \Box), **3**cBr (\bullet , \bigcirc), and **4**cBr (\blacktriangle , \triangle) at 25 °C. The closed and open symbols denote nonaqueous and aqueous solvents, respectively. A, E, M, T, and HFIP stand for acetone, ethanol, methanol, 2,2,2-trifluoroethanol, and 1,1,1,3,3,3-hexafluoro-2-propanol, respectively, and the preceding numbers mean vol %, whereas 50T, 70T, 97T, and 97HFIP are mixtures with water in wt %. The plots of 2Br and 4cBr are shifted by 2 units downward and 4 units upward, respectively, for clarity. For $Y_{\rm Br}$ values, see refs 5b and 9c.

investigation of the above possibilities, since they give no elimination products and β -hydrogens are somewhat hindered to the Br ϕ nsted base-type solvation. It was also supposed that the extent of ion-pair return would be almost similar to the parent 1-bromoadamantane (1Br). Figure 5 shows the GW plot against $Y_{\rm Br}^{5b,9a,c}$ for the rates of solvolysis of 1-bromo-3,5,7-trimethyl-, 1-bromo-3,5,7triisopropyl-, and 1-bromo-3,5,7-tripropyl-adamantanes (2Br, 3cBr, and 4cBr, respectively).

The GW plot for 2Br shows fairly good linear relationship. However, the data points for aqueous ethanol (80E, 70E, 50E, and 30E) obviously fall slightly below the straight line that passes through the points for nonaqueous solvents (100E, 100M, 97T, 97HFIP, 60T-40E, 80T-20E) (m = 0.99, r = 0.999). This trend is more marked for 3cBr and 4cBr. Their rates in nonaqueous solvents show good linear relations: m = 0.99 and r = 0.999 for **3c**Br and m = 1.00 and r = 0.999 for **4c**Br.

Similarly to nonaqueous solvents, methanol and aqueous methanol solvents also give good linear relations, but with smaller *m* values; m = 0.78 (r = 0.999) and m =0.80 (r = 0.999) for **3**cBr and **4c**Br, respectively. A linear extrapolation of the aqueous methanol line for 3cBr in Figure 5 to the $Y_{\rm Br}$ value $(4.44)^{9a}$ for water suggests the rate constant of 3cBr in water of approximately 0.006 s^{-1} at 25 °C, which gives the **3c**Br/**1**Br rate ratio of ~0.8.²⁴ We assume that the Br ϕ nsted-base type hydration to the β -hydrogens is so sensitive to steric encumbrance that more congested **3c**Br is subject to less effective hydration than **1**Br in the transition state for ionization.

The notion of preferential solvation on the cation side has long been suggested,^{7,25} but has not been clearly demonstrated in the GW type relationship. Aqueous ethanol solvents show such a sign. The GW plot of the rate data for 3cBr in aqueous ethanol shows a greater downward dispersion than in aqueous methanol, and the line connecting EtOH, aq ethanol mixtures, and water points obviously results in a downward bulge. This behavior may be due to the hydrophobic interaction of the highly alkylated structure with ethanol in aqueous ethanol. Presumably, the first solvation shell contains more ethanol and less water than the bulk phase, making the ionization less easy.

Previously, Wepster and co-workers found that the Hammett σ constants of bulky alkyl groups, such as *tert*butyl and 1,1-diethylpropyl (Et3C), become significantly more minus in aqueous ethanol or aqueous tert-butyl alcohol than in water, and the results were ascribed to the hydrophobic effect.²⁶ They reported that dispersions in various Hammett relations for the systems having bulky alkyl groups in aqueous organic solvents could be markedly improved by incorporation of an " $h\pi$ " term, where π is Hansch's hydrophobic constant.²⁷ In the present solvolyses, a plot of $log(k_{70E-30W}/k_{60T-40E})$ for the eight substrates included in Tables 3-5 for the two solvents (70E-30W and 60T-40E) having comparable $Y_{\rm Br}$ values (0.68^{9a} and 0.436^{9c}, respectively) against the total value of hydrophobic parameters for substituents²⁷ $(\Sigma \pi)$ is roughly linear (excluding the data point for 1-bromo-3-nonyladamantane) with a negative slope (see Supporting Information).

Recently, the effects of added ethanol on the rates of the benzoin condensation, Diels-Alder reactions, and $S_N 2$ reactions in aqueous solutions have been extensively studied by Breslow and co-workers, and the important role of ethanol as "antihydrophobic agent" has been pointed out.²⁸ The nearly linear behavior of aqueous methanol solvents (Figure 5) is in line with the notion that methanol is a much less effective antihydrophobic agent than ethanol. This is in accord with the much smaller microscopic hydrophobicity parameter for a methyl group (0.41) than that for an ethyl group (0.73); the parameters were obtained from the accelerating effects of added $RNMe_3^+X^-$ (R = Me or Et) on the rate of hydrolysis of *p*-nitrophenyl laurate.²⁹

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⁽²⁴⁾ The reported rate constant of 1Br in water 9a of 7.7 \times 10 $^{-3}$ s $^{-1}$ and the estimated one for 3cBr of $6 \times 10^{-3} s^{-1}$ (see text) were used.

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Table 6. Contributions of the Enthalpy and EntropyTerms of Activation in the Solvolysis of 1Br, 3cBr, and4cBr in 80% EtOH at 25.0 °C^a

	compound		
term	$1\mathbf{Br}^{b}$	$3cBr^{c}$	$4cBr^{c}$
ΔH^{\ddagger}	24.5	25.2	25.8
$-T\Delta S^{\ddagger}$	1.8	0.8	1.0
ΔG^{\ddagger}	26.3	26.0	26.8

 a All values are in kcal mol $^{-1}$. b The data were taken from ref 9a. c See footnote to Table 3.

The similar product patterns for **1**Br and **3**cBr indicate that the introduction of the isopropyl groups may not induce much change in the structure of ion pairs and also the solvent composition around the C(1) cationic carbon and the Br⁻ counterion. However, there might be significant difference in solvent composition around the hydrophobic hydrocarbon moiety between 1Br and 3cBr in the transition state of ionization. The extent of ion pair return would also be assumed to be similar between 1Br and **3c**Br because of structural similarity and insignificant difference in solvolytic reactivity. It would not be reasonable to ascribe the decreased solvolytic reactivity of 3cBr and 4cBr in aqueous ethanol to possible increase in ion pair return, since the ion pair return is expected to decrease in aqueous ethanol that is more nucleophilic than fluorinated alcohols.³⁰

4. Enthalpy and Entropy of Activation. The contributions of the enthalpy and entropy terms of activation for the solvolysis of **1**Br, **3**cBr, and **4**cBr in 80% EtOH are summarized in Table 6.

The ΔH^{\ddagger} value (kcal mol⁻¹) changes in the manner **1**Br (24.5) < **3c**Br (25.8) > **4c**Br (25.2). This trend is similar to that for ΔG^{\ddagger} , **1**Br (26.3) < **3c**Br (26.8) > **4c**Br (26.0). Clearly, the introduction of the three *n*- or isopropyl substituents is unfavorable by 1.3 or 0.7 kcal mol⁻¹ with respect to the ΔH^{\ddagger} term, but favorable by about 1 kcal mol⁻¹ regarding the $-T\Delta S^{\ddagger}$ term. The former effect may be explained by assuming the decreased stability of the cation side in more ethanolic solvation shell with increased hydrophobicity, and the latter by the concomitant decrease in the fraction of water that would be sterically more easily solvating than ethanol at the transition state.

5. Behavior of Mono- and Dialkyl-1-bromoadamantanes in the Grunwald-Winstein Relationship. The greater dispersions in the GW plots for 3,5,7-trialkyl-1-bromoadamantanes, 3cBr and 4cBr, than 2Br (Figure 5) indicate that the carbon number is a more important factor than the shape of the alkyl group. To examine if a n-nonyl group exerts an effect similar to that of the three *n*-propyl groups of **4c**Br, **5**Br was subjected to solvolysis. In this investigation, only five solvents were selected. From the plots in Figure 5, it appears convenient to examine downward dispersions of the data points for 80% EtOH, 70% EtOH, 80% MeOH from a line connecting those for 80% TFE-20% EtOH and 60% TFE-40% EtOH. In Figures 6a are shown the GW plots for 3-isopropyl-, 3-propyl-, and 3-nonyl-1-bromoadamantanes (3aBr, 4bBr, and 5Br, respectively). Evidently, the nonyl group causes only slightly greater dispersions than the propyl group, suggesting that the solvent composition at the place distant from the adamantyl moiety has es-



Figure 6. Plots of log *k* values against Y_{Br} for the solvolysis of (a) **3a**Br (**I**), **4a**Br (**O**), and **5**Br (**A**), and (b) **3b**Br (**I**) and **4b**Br (**O**) at 25 °C. The data points for **4a**Br and **4b**Br, and those for **5b** are shifted downward by 2 and 4 units, respectively, for clarity.

sentially no influence. As shown in Figure 6b for the GW plot for **3b**Br and **4b**Br, both bromides exhibit similar dispersions whose deviations are between their monoand trisubstituted homologues.

Conclusions

FT ICR experiments showed that the introduction of three methyl or three isopropyl substituents into the 3-, 5-, and 7-positions of 1-admantyl cation increases the stability of the cation in the gas phase. The experimental standard Gibbs energy changes of the cation formation (reaction) were in very good agreement with PM3 calculations. However, 1-bromo-3,5,7-trimethyladamantane (2Br) solvolyzes slower than 1-bromoadamantane (1Br) in all the nonaqueous alcoholic solvents examined. The faster rate of **1**Br has been ascribed to the Br ϕ nsted basetype solvation toward relatively positive hydrogen atoms on the 3-, 5-, and 7-positions in the transition state of ionization. When isopropyl or propyl groups are introduced in place of the methyl groups to give **3c**Br or **4c**Br, respectively, the respective rate ratio to 1Br in nonaqueous alcoholic solvents increases to 12–15 or 2–4, owing to the greater electron-donating abilities of the substituents than the methyl group. However, the rate ratios, 3cBr/1Br and 4cBr/1Br, in aqueous organic solvents showed a trend to decrease with increase in the amount of water, reaching 0.84 and 0.15, respectively, in 60% ethanol. In the long history of solvolysis studies, "80% ethanol" has been used as a convenient solvent. However, the present data suggest that aqueous ethanol might result in a wrong conclusion regarding the stability of incipient carbocations and electron-donating ability of alkyl substituents. It is recommended that whenever the solvolytic reactivity is to be related with carbocation stability, the rates should be examined in nonaqueous solvents such as ethanol, methanol, TFE, TFE-EtOH, and 97% HFIP.

Because of unexpectedly decreased rates of solvolysis of alkylated 1-bromoadamantanes having isopropyl or propyl substituents relative to 1Br in aqueous organic

⁽³⁰⁾ An examination of ion pair return by using the chloroformate of **3c**OH was attempted, but it was too unstable for isolation. For the use of the chloroformate of **1**OH, see, Kevill, D. N.; Kyong, J. B.; Weitl, F. L. *J. Org. Chem.* **1990**, *55*, 4304–4311.

solvents, those data points for **3c**Br and **4c**Br show downward dispersions in the Grunwald–Winstein (GW) relationship. In contrast to aqueous ethanol, aqueous methanol mixtures do not show an appreciable downward bulge in the GW plot. Linear extrapolation of the aqueous methanol line to the $Y_{\rm Br}$ value for water (4.44) suggests the rate ratio **3**cBr/**1**Br of ~0.8. It is assumed that the Br ϕ nsted-base type hydration to the β -hydrogens is so sensitive to steric encumbrance that more congested **3c**Br is subject to less effective hydration than **1**Br in the transition state of ionization. This type of solvation by methanol and larger molecules may not be so significant as water since the GW plot for the nonaqueous solvents shows a very good linear relation with $Y_{\rm Br}$.

The markedly slower rates of solvolysis of **3c**Br and **4c**Br in aqueous ethanol and aqueous acetone than in nonaqueous organic solvents having a same $Y_{\rm Br}$ value may be explained by hydrophobic interaction of the highly alkylated structure with the organic component in the aqueous organic mixtures. The first solvation shell containing greater amounts of the organic component than the bulk phase would make the ionization less easy. The present markedly decelerated solvolysis of **3c**Br and **4c**Br in aqueous organic solvents is a kinetic version of anomalously diminished dissociation of alkylbenzoic acids in aqueous ethanol and aqueous *tert*-butyl alcohol that was demonstrated by Wepster and co-workers a decade ago and ascribed to hydrophobic effects.

Experimental Section

Melting points are uncorrected. ¹H NMR spectra were recorded at 270 or 400 MHz. ¹³C NMR spectra were recorded at 67.5, 75.5, or 100 MHz. The spectral data for all new compounds are summarized in the Supporting Information. GLC analyses were conducted on a PEG 20M column (3 mm imes 2 m) or a PEG 20 M capillary column (0.22 mm imes 25 m). Mass spectra were recorded on a GC-MS spectrometer. Elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. 1-Bromo-3,5,7-trimethyladamantane (2Br),^{1a,c,f} 1-bromo-3-isopropyladamantane (3aBr),^{1b,c} 3-isopropyl-1-adamantanol (3aOH),¹¹ 3,5-diisopropyl-1-adamantanol (3bOH),11 and 1-bromo-3-propyladamantane (4aBr)10 were reported previously. 1-Propyladamantane (4aH), 10,31 which had been synthesized by the Wolff-Kishner reduction of 1-(1-adamantyl)-2-propanone,10 was prepared by the direct alkylation of 1Br with PrMgBr in CH2Cl2.12 Solvolysis solvents were purified by previously described methods.³² Anhydrous solvents used for synthesis were purified by the standard procedures. 2,6-Lutidine was distilled over CaH2. Other commercially available reagents were of a reagent-grade quality and used as received. Medium-pressure liquid chromatography (MPLC) was conducted on Merck silica gel 60 (230-400 mesh). Recycle preparative HPLC was performed with GPC columns (JAIGEL 1Ĥ and 2H, 20×600) using CHCl₃ as eluent.

3,5-Diisopropyl-1-adamantanecarboxylic Acid (3b-CO₂H). To a mixture of CCl₄ (80 mL) and H₂SO₄ (100 mL) was added with stirring a solution of 3,5-diisopropyl-1-adamantanol¹¹ (3bOH) (4.92 g, 20.8 mmol) in formic acid (70 mL, 1.8 mol) over 210 min at 8–17 °C by cooling in an ice–water bath. The reaction mixture was poured into ice–water and extracted with CCl₄. The aqueous layer was extracted with CCl₄, and the organic layer was dried (MgSO₄). Evaporation of solvent gave **3b**CO₂H as a colorless solid (5.55 g) in 100% yield: mp 81.0–82.0 °C (from hexane). Anal. Calcd for C₁₇H₂₈O₂: C, 77.22; H, 10.67. Found: C, 76.96; H, 10.58.

1-Bromo-3,5-diisopropyladamantane (3bBr). To a chilled solution of **3b**OH (0.96 g, 4.06 mmol) in benzene (6.0 mL) was added PBr₃ (0.30 mL, 3.16 mmol) in benzene (6.0 mL) over 2 min. The mixture was stirred for 55 min at 0 °C, 18 min at r.t. and then refluxed for 2 h. The reaction mixture was diluted

with ether and then washed with water and saturated NaHCO₃ and dried (MgSO₄). Evaporation of ether and purification by MPLC (SiO₂) gave **3b**Br (0.46 g) as a viscous oil in 38% yield. Anal. Calcd for $C_{16}H_{27}Br$: C, 64.21; H, 9.09. Found: C, 64.39; H, 8.83.

3,5-Diisopropyl-1-adamantanecarbonyl Chloride (3b-COCl). Thionyl chloride (3.10 mL, 43.3 mmol) was slowly added to **3b**CO₂H (1.60 g, 6.05 mmol), and then the mixture was warmed with stirring at 70 °C for 2 h. Excess thionyl chloride was distilled off to give essentially pure **3b**COCl (1.69 g) as a yellow oil in 98% yield, which was used for the next step without further purification.

2-(3,5-Diisopropyl-1-adamantyl)-2-propanol (6). A solution of **3b**COCl (1.69 g, 5.97 mmol) in anhydrous diethyl ether (50 mL) was added over 30 min to methylmagnesium iodide which had been prepared from methyl iodide (2.1 mL, 34 mmol) and magnesium turnings (0.85 g, 35 mmol) in anhydrous diethyl ether (25 mL), and then the mixture was refluxed for 4 h. The reaction mixture was treated with saturated NH₄-Cl and worked up as usual to afford essentially pure **6** (1.63 g) as a yellow oil in 98% yield. HRMS (FAB+) calcd for $C_{19}H_{34}O$ 278.2610, found 278.2609.

3,5,7-Triisopropyl-1-adamantanol (3cOH). Following the procedure reported for the preparation of **3a**OH and **3b**OH,¹¹ trifluoroacetic acid (26.0 mL, 337 mmol) was added with stirring to **6** (1.54 g, 5.53 mmol), and the reaction mixture was stirred at 65 °C for 4 h. To the stirred mixture was added saturated aqueous Na₂CO₃ (170 mL) dropwise. During the addition, a reddish brown oil separated, and its color changed to yellow when 90 mL of saturated aqueous Na₂CO₃ was added. The reaction mixture was refluxed for 3.5 h and then extracted with diethyl ether. The extract was washed with H₂O and dried (MgSO₄) and the solvent evaporated. The residue was subjected to MPLC (hexane–ether) to give **3c**OH (0.88 g) as slowly solidifying, colorless crystals in 57% yield: mp 81.5–82.5 °C. Anal. Calcd for C₁₉H₃₄O: C, 81.95; H, 12.31. Found: C, 81.66; H, 12.22.

1-Bromo-3,5,7-triisopropyladamantane (3cBr). To a solution of **3c**OH (0.81 g, 2.91 mmol) in anhydrous benzene (10 mL) was added a solution of PBr₃ (0.90 g, 9.5 mmol) in anhydrous benzene (10 mL) over 3 min at 0 °C. The reaction mixture was stirred at r.t. for 0.5 h and then refluxed for 2.5 h. The reaction mixture was poured into ice and extracted with diethyl ether. The extract was washed with saturated aqueous NaHCO₃ and dried (MgSO₄), and the solvent was evaporated to give **3c**Br (0.85 g) as slowly solidifying, pale yellow crystals in 86% yield: mp 40.0–40.5 °C. Anal. Calcd for C₁₉H₃₃Br: C, 66.85; H, 9.74. Found: C, 66.56; H, 9.85.

1-Propyladamantane (4aH). This known compound¹⁰ was prepared by a different method¹² than that used originally. A solution (50 mL) of 2.24 mol L^{-1} propylmagnesium bromide in ether was placed in a 300 mL flask, and the ether was distilled off until the residual PrMgBr became white crystals. A solution of 1-bromoadamantane (1Br) (12.1 g, 56.4 mmol) in dry CH₂Cl₂ (134 mL) was added, and the mixture was refluxed under N₂ for 15 h. The reaction mixture was worked up in a usual manner to give an oil (9.25 g), which on treatment by MPLC (hexane) gave **4a**H as a colorless oil (6.45 g) in 64% yield.

1,3-Dipropyladamantane (4bH). Treatment of **4a**Br (7.93 g, 30.8 mmol) with propylmagnesium bromide (63 mmol) in CH₂Cl₂ (70 mL) in the manner described for **4a**H gave crude **4b**H (6.34 g) as a yellow oil, which was then purified by MPLC (hexane). Anal. Calcd for C₁₆H₂₈: C, 87.36; H, 12.92. Found: C, 87.19; H, 12.81.

1-Bromo-3,5-dipropyladamantane (4bBr). A mixture of **4b**H (500 mg, 2.26 mmol) and Br_2 (2.3 mL, 45 mmol) in CCl₄ (45 mL) was refluxed for 18 h. The reaction mixture was treated as usual to give a yellow oil, which was purified by MPLC (hexane) to give **4b**Br (480 mg) in 71% yield. Anal. Calcd for C₁₆H₂₇Br: C, 64.21; H, 9.09. Found: C, 64.13; H, 9.23.

1,3,5-Tripropyladamantane (4cH). Treatment of **4b**Br (9.71 g, 32.4 mmol) with propylmagnesium bromide (72 mmol) in CH_2Cl_2 (50 mL) in the manner described for **4a**H gave crude

4cH (7.5 g) as a yellow oil, which was shown by GLC to contain about 30% of **4c**H and 60% of **4b**H. Treatment of the mixture by MPLC (hexane) afforded fractions containing **4b**H and **4c**H, which were not investigated further. Treatment of a fraction by GPC gave pure **4c**H. Anal. Calcd for $C_{19}H_{34}$: C, 86.95; H, 13.05. Found: C, 86.97; H, 12.76.

1-Bromo-3,5,7-tripropyladamantane (4cBr). A mixture of **4c**H (174 mg, 0.66 mmol) and Br_2 (0.4 mL, 7.8 mmol) in CCl_4 (0.1 mL) was refluxed for 39 h. The reaction mixture was treated as usual to give a yellow oil, which was purified with GPC to give **4c**Br (135 mg) in 60% yield. The elemental analysis data were unsatisfactory because of difficulty in complete removal of solvent. Anal. Calcd for $C_{19}H_{33}Br$: C, 66.85; H, 9.74. Found: C, 65.82; H, 9.71.

1-Nonyladamantane (5H). Treatment of **1**Br (300 mg, 1.40 mmol) with nonylmagnesium bromide (2.9 mmol) in CH_2Cl_2 (6 mL) at reflux for 12 h followed by usual work up gave **5**H (220 mg) in 59% yield after purification by MPLC (hexane). Anal. Calcd for $C_{19}H_{34}$: C, 86.95; H, 13.05. Found: C, 86.80; H, 13.33.

1-Bromo-3-nonyladamantane (5Br). A mixture of **5**H (2.83 g, 10.8 mmol) and Br₂ (5 mL, 98 mmol) in CCl₄ (5 mL) was heated at 70 °C for 12 h. The reaction mixture was treated as usual to give a yellow oil, which was purified with a SiO₂ column (hexane) to give **5**Br (2.95 g) as a yellow oil in 80% yield. Calcd for $C_{16}H_{27}Br$: C, 66.85; H, 9.74. Found: C, 66.40; H, 9.99

FT ICR Experiments. Typically, mixtures of two carefully degassed bromides, R_1Br and R_2Br , with total pressures in the range 5×10^{-7} to 2×10^{-6} mbar were introduced into the high vacuum section of a modified Bruker CMS-47 Fourier Transform ICR mass spectrometer^{13a} and subjected to electron ionization under mild conditions (nominal energies of 11–12 eV). Ions R_1^+ and R_2^+ thus obtained were allowed to react and equilibrate, the reaction being monitored for some 20 s, with samplings every 1-2 s. The ratios of the partial pressures of the neutral reagents were varied as much as possible. At least six different experiments were performed for each couple R_1 -

 Br/R_2Br . In all cases, double-resonance-like experiments were performed in order to confirm the exchange of bromide anion.

Kinetic Methods. The preparation of solvents and kinetic studies followed the methods described previously.³²

Product Studies. The solutions of 0.01 and 0.005 mol L⁻¹ of **1**Br and **3c**Br, respectively, in 80% ethanol–20% water containing 0.025 mol L⁻¹ 2,6-lutidine were kept at 25 or 75 °C. The solvolyses at 75 °C were carried out for 10 half-lives, but those at 25 °C were conducted for 1.5 and 2.9 half-lives for 1Br and **3c**Br, respectively. The reaction solutions were treated with solid K₂CO₃, and the organic layer separated by salting-out was dried over Drierite and subjected to GLC analysis using a PEG 20M capillary column and an FID detector. The calibration of the peak area was performed by using factors 0.83 for **1**OEt vs **1**OH and 0.90 for **3c**OEt vs **3c**OH.

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Supporting Information Available: Estimations of ΔH^- (3,theor) of **4c**⁺ and the rate constant of ethanolysis of **1**Br, plot of log($k_{70E-30W}/k_{60T-40E}$) vs $\Sigma \pi$, and NMR data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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