

The S_N2-S_N1 Spectrum. 4. The S_N2 (Intermediate) Mechanism for Solvolyses of *tert*-Butyl Chloride: A Revised Y Scale of Solvent Ionizing Power Based on Solvolyses of 1-Adamantyl Chloride^{1,2}

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Abstract: Kinetic data are reported for solvolyses of 1-adamantyl chloride (I, X = Cl) in acetic, formic, and trifluoroacetic acids, water, and binary aqueous mixtures with acetone, ethanol, methanol, and trifluoroethanol. Additional kinetic data for solvolyses of 1-adamantyl bromide are also reported. Correlations of logarithms of solvolysis rates for 1-adamantyl chloride (or bromide) with rates for *tert*-butyl chloride (or bromide) show significant deviations for weakly nucleophilic media (acetic, formic, and trifluoroacetic acids, trifluoroethanol/water, and hexafluoroisopropyl alcohol/water). Relative rates (1-adamantyl/*t*-Bu) vary from ca. 1/3000 in ethanol to ca. 1/3 in 97% hexafluoroisopropyl alcohol/water. Equilibria between stable 1-adamantyl and *tert*-butyl cations (RX + R⁺ ⇌ R⁺ + R⁻X) favor the adamantyl cation and lead to the prediction that S_N1 reactions of 1-adamantyl halides should be more rapid than those of *tert*-butyl halides. This predicted reverse of the usual order is closely approached for solvolyses in the least nucleophilic solvents (e.g., hexafluoroisopropyl alcohol/water), and rate accelerations for solvolyses of *tert*-butyl halides in more nucleophilic solvents are attributed to nucleophilic solvent assistance (S_N2 character). This implies that the Y scale of solvent ionizing power based on *tert*-butyl chloride contains contributions from solvent nucleophilicity. A new scale (Y_{Cl}) based on 1-adamantyl chloride is defined by log (k/k₀)_{1-AdCl} = Y_{Cl}, where k refers to solvolysis rate constants in any solvent at 25 °C and k₀ refers to 80% ethanol/water (v/v). Solvolysis rate constants for *tert*-butyl chloride are accurately correlated by the four-parameter equation: log (k/k₀)_{t-BuCl} = mY_{Cl} + lN, where m is the sensitivity to solvent ionizing power and l is the sensitivity to the solvent nucleophilicity parameter N. These results are explained by the S_N2 (intermediate) mechanism in which a weakly nucleophilically solvated ion pair is formed in the rate-determining step, followed by relatively rapid substitution or elimination to give products. Extensive tabulations of Y_{Cl} and corresponding Y_B values (based on solvolyses of 1-adamantyl bromide) supplement the Y_{OTs} values previously reported and provide suitable parameters for the investigation of a wide variety of solvolytic displacement reactions and other solvent effects for both organic and inorganic substrates.

Solvolyses of *tert*-butyl chloride constitute one of the cornerstones of physical organic chemistry, and generations of students have taught that they are S_N1 processes.³ *tert*-Butyl chloride is the model substrate for the Winstein-Grunwald equation (1),

$$\log (k/k_0) = mY \quad (1)$$

where k is the rate of solvolysis in any solvent relative to k₀ for 80% v/v ethanol/water; m is the response to solvent ionizing power Y, defined by m = 1 for solvolyses of *tert*-butyl chloride at 25 °C.⁴ It is assumed that solvolyses of *tert*-butyl chloride are insensitive to solvent nucleophilicity.⁴ For S_N2 solvolyses, the extended Winstein-Grunwald equation (2)^{2b} or (3) can be used.⁵ In eq

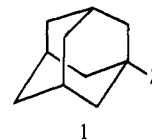
$$\log (k/k_0) = lN + mY \quad (2)$$

$$\log (k/k_0) = c_1d_1 + c_2d_2 \quad (3)$$

2, l measures the response to solvent nucleophilicity N, and in eq 3, d₁ and d₂ are measures of solvent nucleophilicity and electrophilicity, respectively. Again, solvolyses of *tert*-butyl chloride play a key role: l = 0 and m = 1 (eq 2),^{5b} or c₁ = c₂ = 1 (eq 3)^{5a}—the latter (much less widely accepted) assignment implies substantial S_N2 character for solvolyses of *tert*-butyl chloride as advocated

by Swain and Thornton,⁶ whereas l = 0 (eq 2) implies model S_N1 behavior.^{5b,c} These two somewhat conflicting and arbitrary assignments (and other evidence^{7,8} discussed below) raised doubts about the suitability of *tert*-butyl chloride as a model compound and led to the work described here.

We have studied solvolyses of 1-adamantyl chloride (I, X = Cl) in solvents having a wide variety of ionizing powers and nucleophilicities; (I, X = Cl) is commercially available, is relatively



reactive and, importantly, is not capable of undergoing elimination or rear-side nucleophilic attack.⁸ Consequently, it is an excellent substrate for defining a scale of solvent ionizing power for chlorides. Classical studies on the correlation of solvolysis rates utilized aqueous, alcoholic, and weakly acidic media,^{4,5a} which are now known to be relatively nucleophilic.^{2b} Enhanced structural effects on solvolytic reactivity in less nucleophilic media (e.g., trifluoroacetic acid and hexafluoroisopropyl alcohol) are now well established.^{2c,9} Solvolyses of *tert*-butyl chloride in trifluoroethanol were regarded as anomalous because of rate-limiting elimination,^{7,8} but this interpretation has been questioned.^{2d,c} In this paper we show that solvolyses in these weakly nucleophilic, fluorinated media can be related to the classical studies on correlation of solvolysis rates^{4,5a} and to contemporary studies of equilibria between stable

(1) Presented in part at the International Symposium on Chemistry of Carbocations, Bangor, Wales, U. K., September 1981.

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Table I. Rate Constants for Solvolyses of 1-Adamantyl Chloride (I, X = Cl)^a

solvent ^b	temp, °C	<i>k</i> , s ⁻¹	ΔH^\ddagger , kcal/ mol	ΔS^\ddagger , eu	solvent ^b	temp, °C	<i>k</i> , s ⁻¹	ΔH^\ddagger , kcal/ mol	ΔS^\ddagger , eu
80% EtOH	75.1 ^d	(4.7 ± 0.2) × 10 ⁻⁶			H ₂ O ^j	25.0	(3.00 ± 0.12) × 10 ⁻⁴		
	50.0 ^d	(2.6 ± 0.1) × 10 ⁻⁷			70% MeOH	49.9 ^d	(5.9 ± 0.2) × 10 ⁻⁶		
	25.0 ^c	9.1 × 10 ⁻⁹	25.1	-11.2		35.0 ^d	(9.1 ± 0.4) × 10 ⁻⁷	24.1	-7.9
	25.0 ^{c,e}	7.6 × 10 ⁻⁹	25.4	-10.4		25.0 ^c	2.3 × 10 ⁻⁷		
70% EtOH	79.7 ^d	(3.5 ± 0.1) × 10 ⁻⁵			60% MeOH	50.0	(2.20 ± 0.01) × 10 ⁻⁵		
	49.9 ^d	(1.33 ± 0.06) × 10 ⁻⁶	24.2	-10.6		25.0 ^{d,i}	(9.3 ± 0.3) × 10 ⁻⁷	23.6	-6.9
	25.0 ^c	5.2 × 10 ⁻⁸			50% MeOH	50.0 ^{k,l}	(7.7 ± 0.3) × 10 ⁻⁵		
60% EtOH	49.9 ^{d,f}	(4.84 ± 0.12) × 10 ⁻⁶				25.0	(4.0 ± 0.2) × 10 ⁻⁶	22.0	-9.4
	35.0 ^d	(7.5 ± 0.7) × 10 ⁻⁷	24.1	-8.5	40% MeOH	50.0	(2.62 ± 0.03) × 10 ⁻⁴		
	25.0 ^c	1.9 × 10 ⁻⁷				25.0 ^k	(1.43 ± 0.01) × 10 ⁻⁵	21.6	-8.2
50% EtOH	101.7 ^{f,g}	2.69 × 10 ⁻³			30% MeOH	50.0 ^k	(8.04 ± 0.05) × 10 ⁻⁴		
	74.9 ^g	(2.62 ± 0.02) × 10 ⁻⁴				25.0 ^k	(4.31 ± 0.03) × 10 ⁻⁵	21.8	-5.6
	49.7 ^g	(1.78 ± 0.05) × 10 ⁻⁵			20% MeOH	50.1 ^k	(2.06 ± 0.02) × 10 ⁻³		
	25.0 ^c	9.2 × 10 ⁻⁷	22.5	-10.6		25.0 ^k	(1.01 ± 0.04) × 10 ⁻⁴	22.4	-1.6
	25.0 ^{c,h}	1.0 × 10 ⁻⁶	22.2	-11.6	10% MeOH	50.0	(4.3 ± 0.2) × 10 ⁻³		
	25.0 ^{d,i}	(8.3 ± 0.5) × 10 ⁻⁷				25.0	(1.95 ± 0.03) × 10 ⁻⁴	23.0	1.6
40% EtOH	75.0 ^{f,g}	9.4 × 10 ⁻⁴			50% (CH ₃) ₂ CO	50.0	(8.85 ± 0.1) × 10 ⁻⁶		
	49.7 ^{f,g}	8.05 × 10 ⁻⁵				25.0 ^d	(4.3 ± 0.2) × 10 ⁻⁷	22.6	-12.0
	29.9 ^g	(8.5 ± 0.1) × 10 ⁻⁶			40% (CH ₃) ₂ CO	50.1	(4.15 ± 0.08) × 10 ⁻⁵		
	25.0 ^c	4.7 × 10 ⁻⁶	21.2	-11.7		25.0 ^l	(2.27 ± 0.11) × 10 ⁻⁶	21.5	-12.2
	49.9	(7.75 ± 0.04) × 10 ⁻⁵	21.4	-11.4	30% (CH ₃) ₂ CO	50.1	(2.04 ± 0.01) × 10 ⁻⁴		
	25.0	(4.43 ± 0.02) × 10 ⁻⁶				25.0	(1.31 ± 0.07) × 10 ⁻⁵	20.3	-12.7
30% EtOH	74.5 ^g	(3.41 ± 0.02) × 10 ⁻³			20% (CH ₃) ₂ CO	50.1 ^m	(8.64 ± 0.03) × 10 ⁻⁴		
	49.7 ^g	(3.86 ± 0.05) × 10 ⁻⁴				25.0	(4.69 ± 0.04) × 10 ⁻⁵	21.6	-5.9
	29.9 ^{f,g}	4.71 × 10 ⁻⁵			10% (CH ₃) ₂ CO	50.0 ^m	(2.92 ± 0.05) × 10 ⁻³		
	25.0	2.78 × 10 ⁻⁵	19.5	-14.1		25.0	(1.51 ± 0.04) × 10 ⁻⁴	22.1	-1.9
	74.8	(3.3 ± 0.2) × 10 ⁻³	19.3	-14.7	5% (CH ₃) ₂ CO	50.0 ^k	(5.06 ± 0.08) × 10 ⁻³		
	59.6	(9.43 ± 0.09) × 10 ⁻⁴				25.0	(2.21 ± 0.03) × 10 ⁻⁴	23.4	3.1
	49.9	(3.88 ± 0.05) × 10 ⁻⁴			<0.5% (CH ₃) ₂ CO	50.1	(8.1 ± 0.1) × 10 ⁻³		
	25.0	(2.72 ± 0.05) × 10 ⁻⁵				25.0 ^k	(2.98 ± 0.09) × 10 ⁻⁴	24.6	7.7
20% EtOH	49.7 ^g	(1.49 ± 0.04) × 10 ⁻³			CH ₃ CO ₂ H	75.1 ⁿ	(2.8 ± 0.1) × 10 ⁻⁷	(29) ^o	(-6) ^o
	29.9 ^g	(1.80 ± 0.04) × 10 ⁻⁴				25 ^{c,o}	2 × 10 ⁻¹⁰		
	25.0 ^c	1.02 × 10 ⁻⁴	20.2	-9.1	HCO ₂ H	25.0 ^p	(1.28 ± 0.02) × 10 ⁻⁵		
	49.9	(1.52 ± 0.01) × 10 ⁻³	20.6	-7.9	97% CF ₃ CH ₂ OH	75.2 ^k	(7.65 ± 0.3) × 10 ⁻⁴		
	25.0	(9.6 ± 0.2) × 10 ⁻⁵				49.7	(7.66 ± 0.03) × 10 ⁻⁵	19.8	-16.4
10% EtOH	49.7 ^g	(3.62 ± 0.14) × 10 ⁻³				25.0 ^q	(5.41 ± 0.08) × 10 ⁻⁶		
	29.9 ^g	(3.97 ± 0.02) × 10 ⁻⁴			70% CF ₃ CH ₂ OH	75.2 ^l	1.40 × 10 ⁻³		
	25.0 ^c	2.18 × 10 ⁻⁴	21.1	-4.4		49.6	(1.26 ± 0.02) × 10 ⁻⁴	20.9	-11.8
	49.9	(3.83 ± 0.04) × 10 ⁻³	22.2	-1.1		25.0 ^q	(7.34 ± 0.01) × 10 ⁻⁶		
	25.0	(1.97 ± 0.03) × 10 ⁻⁴			50% CF ₃ CH ₂ OH	25.0 ^q	(1.16 ± 0.05) × 10 ⁻⁵		
5% EtOH	49.9	(5.10 ± 0.09) × 10 ⁻³			CF ₃ CO ₂ H	25.0 ^r	ca. 3 × 10 ⁻⁴		
	25.0	(2.6 ± 0.1) × 10 ⁻⁴	22.2	-0.3					

^a Determined conductimetrically in duplicate except where otherwise noted; errors shown are average deviations. ^b Percent EtOH refers to percent ethanol/water (v/v), percent MeOH refers to percent methanol/water (v/v), percent (CH₃)₂CO refers to percent acetone/water (v/v), percent fluorinated alcohol refers to percent fluorinated alcohol/water (w/w). ^c Calculated from data at other temperatures. ^d Determined titrimetrically in duplicate usually with added lutidine. ^e Reference 12a. ^f One result determined conductimetrically. ^g Independent measurements by T.W.B. (Princeton, 1971). ^h Reference 12b. ⁱ No lutidine present. ^j Containing <0.1% EtOH; see also data for <0.5% (CH₃)₂CO/water. ^k Triplicate determination. ^l One additional result determined titrimetrically. ^m Quadruplicate determination. ⁿ Buffered with 0.01 M sodium acetate and titrated potentiometrically with *p*-toluenesulfonic acid in acetic acid. ^o Estimated from four kinetic runs at 85–125 °C (Volhard titration, 0.025 M substrate, 0.03 M sodium acetate), using a batch of acetic acid giving rate constants too high-adventitious water apparently led to improved infinity titers and to more reliable results at high temperatures. ^p Lithium carbonate added to give 0.05 M formate buffer and 0.025 M water (0.03 M substrate) aliquots quenched in acetic acid, and halide concentration determined by Volhard titration. ^q The following results were obtained for solvolyses of *tert*-butyl chloride in the same solvent batches: 97% CF₃CH₂OH, 25 °C, *k* = (1.34 ± 0.03) × 10⁻⁴ (lit. 1.319 × 10⁻⁴, ref 7a); 50 °C, *k* = (1.92 ± 0.08) × 10⁻³, ΔH^\ddagger = 19.7 kcal/mol, ΔS^\ddagger = -10.1 eu; 70% CF₃CH₂OH, 25 °C, *k* = 4.20 × 10⁻⁴ (lit. 4.27 × 10⁻⁴, ref 7a); 50% CF₃CH₂OH, 25 °C, *k* = (1.53 ± 0.04) × 10⁻³. ^r Estimate based on <20% reaction and the theoretical infinity—the reaction is reversible even when buffered; 0.05 M sodium carbonate added to give 0.1 M trifluoroacetate buffer—also 0.1 M (CF₃CO)₂O added; aliquots (1 mL) quenched in acetic acid (10 mL), and halide concentration determined by Volhard titration. Three determinations for *tert*-butyl chloride at 0 °C gave (5 ± 0.5) × 10⁻⁵; i.e., if ΔH^\ddagger is in the range 16–19 kcal/mol, *k* = 7–10 × 10⁻⁴ at 25 °C, in satisfactory agreement with the literature value of 6.4 × 10⁻⁴ (ref 12c).

carbocations.^{10,11} A simple, consistent interpretation emerges that, strikingly, is not in accord with the S_N1 mechanism for solvolyses of *tert*-butyl halides.

Results

New kinetic data for solvolyses of 1-adamantyl chloride (I, X = Cl) are shown in Table I and for 1-adamantyl bromide (I, X = Br) in Table II. Reactions were studied conductimetrically and/or titrimetrically depending on the solvent and on reaction

half-life. For some reactions in less aqueous alcohols, further reaction between HBr or HCl and alcohols became significant, and it was necessary either to use theoretical infinity titers^{12a} or to buffer the solution (e.g., with 2,6-lutidine). Even buffered

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Table II. Rate Constants for Solvolyses of 1-Adamantyl Bromide (I, X = Br) and Bromide/Chloride Rate Ratios at 25 °C^a

solvent ^b	k , s ⁻¹	Br/Cl ratio ^e	
		1-AdX	<i>t</i> -BuX
80% EtOH ^{d,f,g}	$(2.8 \pm 0.1) \times 10^{-7}$	35 ^h	39
60% EtOH ⁱ	$(5.1 \pm 0.1) \times 10^{-6}$	27	31
50% EtOH ^j	$(2.12 \pm 0.10) \times 10^{-5}$	26	30
40% EtOH ^k	$(1.17 \pm 0.03) \times 10^{-4}$	26	29
30% EtOH	$(6.98 \pm 0.02) \times 10^{-4}$	26	26 ^l
20% EtOH	$(2.31 \pm 0.02) \times 10^{-3}$	24	25 ^l
10% EtOH	$(4.12 \pm 0.05) \times 10^{-3}$	21	27 ^l
H ₂ O ^m	$(7.7 \pm 0.3) \times 10^{-3}$	26	25 ^l
70% MeOH ⁿ	$(7.3 \pm 0.2) \times 10^{-6}$	32	37
60% MeOH	$(3.1 \pm 0.1) \times 10^{-5}$	33	33
50% MeOH	$(1.14 \pm 0.02) \times 10^{-4}$	29	31 ^l
40% MeOH	$(3.90 \pm 0.05) \times 10^{-4}$	27	29 ^l
30% MeOH	$(1.13 \pm 0.01) \times 10^{-3}$	26	26 ^l
20% MeOH	$(2.46 \pm 0.07) \times 10^{-3}$	24	26 ^l
10% MeOH	$(4.1 \pm 0.1) \times 10^{-3}$	21	27 ^l
60% (CH ₃) ₂ CO ^o	$(3.0 \pm 0.1) \times 10^{-6}$		47
50% (CH ₃) ₂ CO ^p	$(1.55 \pm 0.04) \times 10^{-5}$	36	41
40% (CH ₃) ₂ CO	$(7.80 \pm 0.05) \times 10^{-5}$	34	35 ^l
30% (CH ₃) ₂ CO	$(3.62 \pm 0.08) \times 10^{-4}$	28	31 ^l
20% (CH ₃) ₂ CO	$(1.29 \pm 0.03) \times 10^{-3}$	28	27 ^l
10% (CH ₃) ₂ CO	$(3.15 \pm 0.09) \times 10^{-3}$	21	23 ^l
CH ₃ CO ₂ H ^{q,d,a}	2.1×10^{-9}	10	14
HCO ₂ H ^r	8.25×10^{-5}	6	9
97% CF ₃ CH ₂ OH ^r	9.5×10^{-5}	18	22 ^s
70% CF ₃ CH ₂ OH	$(1.71 \pm 0.02) \times 10^{-4}$	23	26 ^t
50% CH ₃ CH ₂ OH	$(3.1 \pm 0.2) \times 10^{-4}$	27	23
97% (CF ₃) ₂ CHOH ^u	9.1×10^{-3}	9 ^u	9 ^u

^{a-d} Same as Table I. ^e 1-Adamantyl data from Tables I and II and *tert*-butyl data from ref 4b and 12e (unless stated otherwise). ^f Data at other temperatures: k , °C; $(8.46 \pm 0.05) \times 10^{-6}$, 50.15; $(1.25 \pm 0.06) \times 10^{-4}$, 75.1; $\Delta H^\ddagger = 24.5$ kcal/mol; $\Delta S^\ddagger = -6.2$ eu. ^g Literature values, 10⁷ k : 4.4;^{12a} 5.1;⁸ 1.16;^{12f} 1.8.^{12g} ^h Taking $k = 8 \times 10^{-9}$ s⁻¹ for 1-AdCl (Table IV). ⁱ Literature values, 10⁶ k : 7.19;⁸ 6.52.^{12d} ^j Literature, 10⁵ k : 2.86.^{12d} ^k Literature, 10⁴ k : 1.21.^{12d} ^l Data for *tert*-butyl bromide from ref 14c. ^m Quadruplicate determination—solvent contained <0.1% EtOH; data at other temperatures: k , °C; $(2.6 \pm 0.1) \times 10^{-2}$, 35.0; $(1.5 \pm 0.1) \times 10^{-1}$, 50.0; $\Delta H^\ddagger = 22.2$ kcal/mol; $\Delta S^\ddagger = 6.1$ eu. ⁿ Triplicate determination. ^o Literature, 10⁶ k : 3.57.⁸ ^p Literature, 10⁵ k : 1.84.⁸ ^q As in Table I, footnote *n*; data at other temperatures: k , °C; $(2.46 \pm 0.03) \times 10^{-6}$, 75.1; $(3.46 \pm 0.03) \times 10^{-7}$, 59.6; $\Delta H^\ddagger = 28.5$ kcal/mol; $\Delta S^\ddagger = -2.8$ eu; literature at 25 °C, 10⁹ $k = 2.3$.⁸ ^r Reference 8. ^s Data for *tert*-butyl bromide from ref 13. ^t Data for *tert*-butyl halides; chloride, 4.48×10^{-4} ; bromide 1.15×10^{-2} (this work). ^u Reference 2e.

solutions of acetic acid and particularly of trifluoroacetic acid gave unsatisfactory experimental infinity values because of reversible reactions.^{4b} For most titrimetric kinetic runs, substrate concentrations of ca. 0.005 M were used to minimize complications (e.g., from variation in ionic strength during the reactions). For reactions in highly aqueous media, substrate concentrations were ca. 10⁻⁵ M, and our previously described techniques were used for the preparation of solutions and in data processing.^{14a,c}

To minimize errors from temperature extrapolations, reactions were monitored for long periods (up to 38 days). Infinity values were obtained from reactions at higher temperatures. The results in Table I include only one extrapolation from 75 to 25 °C (CH₃CO₂H), two from 50 to 25 °C (80%, 70% EtOH), and two from 35 to 25 °C (60% EtOH and 70% MeOH). Extrapolated results are usually too high—e.g., see data for 1-adamantyl chloride in 50% EtOH (Table I). Our results for 1-adamantyl bromide (Table II) avoid temperature extrapolations (except for acetic acid) and are, as expected, lower than the extrapolated values previously reported.^{8,12d} The reliability of the results is supported by the consistent activation parameters (Table I) and by the brom-

Table III. Salt Effects on Hydrolysis of 1-Adamantyl Bromide^a

salt added	k , s ⁻¹	% change in k
none ^b	$(2.57 \pm 0.13) \times 10^{-4}$	
0.1 M LiBr	$(2.71 \pm 0.15) \times 10^{-4}$	5.4
0.1 M LiCl	$(2.78 \pm 0.12) \times 10^{-4}$	8.2
0.1 M NEt ₄ Br ^c	$(2.85 \pm 0.08) \times 10^{-4}$	10.9
0.04 M LiClO ₄	$(2.92 \pm 0.22) \times 10^{-4}$	13.6

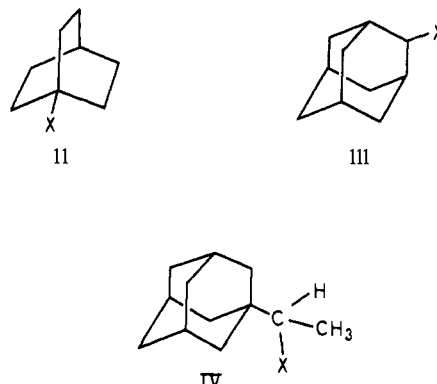
^a In 50% acetone/water (v/v) at 49.9 °C; determined titrimetrically in duplicate. ^b Determined titrimetrically in quadruplicate. ^c One measurement of rate constant.

ide/chloride rate ratios (Table II), which closely parallel the corresponding ratios obtained for solvolyses of *tert*-butyl halides. The effects of added salts on solvolyses of 1-adamantyl bromide are given in Table III.

Discussion

Our mechanistic deductions from the effect of solvent on reactivity are based on a model that takes into account the roles of solvent as nucleophile and electrophile.^{15a} These kinetic effects are analyzed by using linear free-energy relationships and empirical constants derived from the reactivity of appropriate model compounds, and mechanistic deductions are then made.

General Approach and Choice of Model Compounds. A systematic study of various model compounds has been carried out on tosylates. Relative rates of solvolyses of 1-adamantyl (I),^{14b} 1-bicyclo[2.2.2]octyl (II),^{2c} 2-adamantyl (III),^{2c} and 1-



adamantylmethylcarbinyl (IV)^{2c} tosylates and ArCCH₂CF₃OTs (two Ar groups¹⁶) are essentially constant for a range of solvents of widely varying nucleophilicities and ionizing powers. These S_N1 solvolyses are insensitive to solvent nucleophilicity, and any of the four compounds (I–IV) should be a suitable model for a scale of solvent ionizing power. The mechanisms of reaction of I–III are further simplified by the absence of elimination products.⁸ We have defined a scale of solvent ionizing power (Y_{OT}) based on solvolyses of 2-adamantyl tosylate (III, X = OTs).^{2b} Also we have shown by using various correlations (e.g., eq 2) that variable nucleophilic assistance is the key factor influencing the S_N2-S_N1 spectrum of solvolyses.^{2b,c} It has not been necessary to introduce an extra term in eq 2 to account explicitly for variable electrophilic solvent assistance (i.e., solvation of the leaving group^{2b,c}); either it is constant or it is adequately accounted for by using the mY term in eq 2, provided that correlations are restricted to solvolyses of substrates having the same leaving group (e.g., tosylate).^{14a}

Our approach retains desirable features of both Swain and Winstein's classical studies. The push-pull mechanism of Swain emphasizes both nucleophilic and electrophilic assistance,^{5a} and the N-Lim treatment of Winstein emphasizes a mechanistic spectrum.^{4c} We strongly favor experimentally derived empirical constants rather than statistically optimized "constant" parameters; the latter are ill-defined, and new data may be difficult to in-

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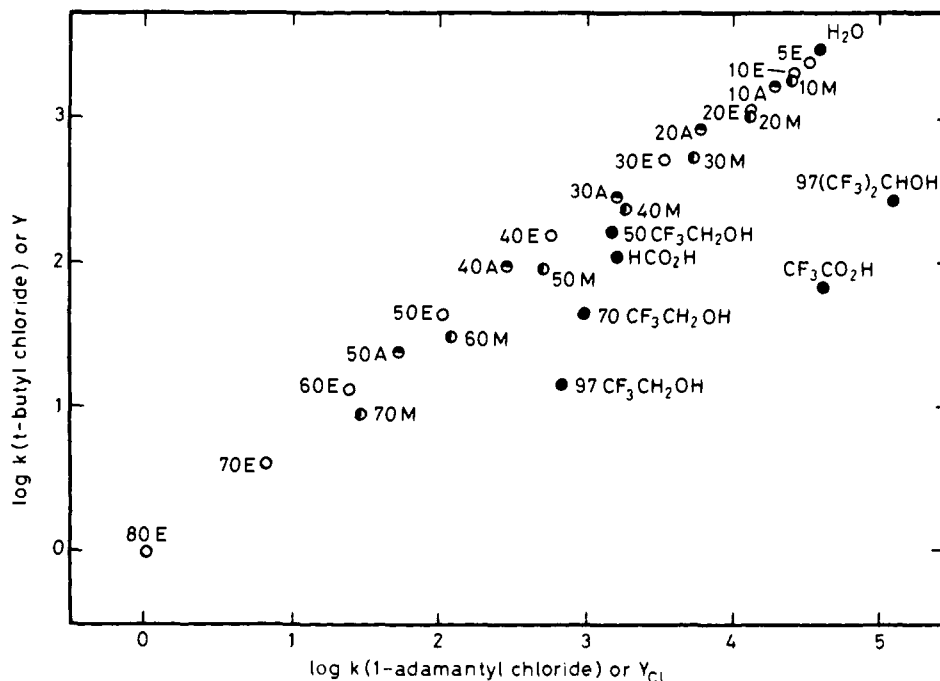


Figure 1. Correlation of logarithms of solvolysis rates for 1-adamantyl chloride (I, X = Cl) vs. *tert*-butyl chloride at 25 °C. Data from Table IV for I, X = Cl, and from Table II and ref 12c for *tert*-butyl chloride.

corporate into the existing framework.^{15a}

We propose to extend our previous work by defining *Y* values for each leaving group from *experimental* data; each of these *Y* scales will be a combination of general solvent ionizing power (or polarity) and specific solvation effects including solvation of the leaving group. Specific solvation of the alkyl part of the substrate will not be allowed for explicitly, but the adamantyl framework will provide a constant alkyl group. In the future it may be possible to dissect reliably the *Y* values into constituent terms, while maintaining a strictly limited number of adjustable parameters (preferably one or two). In the meantime, the availability of *Y* values for each leaving group will emphasize the importance of electrophilic solvent assistance and the need to compare solvolyses of substrates having identical or very similar leaving groups.

Therefore, to replace the *Y* scale based on solvolyses of *tert*-butyl chloride, we required a chloride structurally similar to tosylates I–IV. Experimental convenience determined the final choice of model compound, because the chlorides of II–IV would react inconveniently slowly and/or extrapolation errors would be substantial. 1-Adamantyl chloride (I, X = Cl) is a moderately reactive bridgehead chloride^{15b} that is readily available.^{12a} Extensive kinetic data were already available for solvolyses of 1-adamantyl bromide (I, X = Br).⁸ Consequently, we chose solvolyses of 1-adamantyl halides to define new *Y* scales of solvent ionizing power for halides. Alternative model substrates, structurally different from I–IV, have been considered previously but now appear to be less suitable: e.g., triphenylmethyl chloride is very reactive and undergoes ion-pair return;^{6a} neophyl chloride is a relatively unreactive primary compound,^{15a} which may react by competing nucleophilically solvent-assisted (k_s) and anchimerically assisted (k_A) processes.

Common-ion rate depressions, well established in solvolyses of activated systems (e.g., benzhydryl halides), were insignificant for solvolyses of 1-adamantyl bromide in 50% acetone/water (Table III), as expected from previous studies using EtOH/CF₃CH₂OH and H₂O/CF₃CH₂OH mixtures^{17a} and from analogous results for both 1- and 2-adamantyl tosylates^{2c} and for *tert*-butyl halides.^{17b} Also there is no evidence for a special salt effect with LiClO₄ in these systems (Table III). These results demonstrate the absence of significant external-ion-pair return.

tert-Butyl *p*-nitrobenzoate does *not* undergo ¹⁸O scrambling during solvolysis,¹⁸ and other evidence against appreciable internal-ion-pair return ("hidden return") has been presented elsewhere.^{2c,e} It appears that solvolyses leading to these relatively unstable cations do not involve appreciable ion-pair return. These results contrast with recent data on solvolyses of *p*-methoxybenzyl bromide,¹⁹ which appear to proceed via longer-lived intermediates. Solvolyses of 1-adamantyl bromide are not accelerated by sodium hydroxide, showing that enforced front-side nucleophilic attack is a product step, not a rate-determining step.²⁰ Thus, there are no indications of mechanistic anomalies for solvolyses of 1-adamantyl halides, which appear to be very good models for S_N1 behavior.

Solvent Effects. We now define a scale of solvent ionizing power for chlorides (designated Y_{Cl}) by eq 4, with RCl referring to

$$\log (k/k_0)_{RCl} = mY_{Cl} \quad (4)$$

1-adamantyl chloride ($m = 1$) and where k refers to the rate constant for solvolysis in any solvent at 25 °C and k_0 refers to 80% ethanol/water (v/v). An analogous scale for bromides (Y_{Br}) is defined by using data for 1-adamantyl bromide (eq 5, $m = 1$).

$$\log (k/k_0)_{RBr} = mY_{Br} \quad (5)$$

The new *Y* values are summarized in Table IV, which includes some data estimated by extrapolation or interpolation. A plot of logarithms of solvolysis rates for *tert*-butyl chloride vs. 1-adamantyl chloride is almost linear for aqueous acetone, ethanol, and methanol, with significant deviations for the less nucleophilic media (acetic, formic, and trifluoroacetic acids, trifluoroethanol, and hexafluoroisopropyl alcohol); Figure 1, Table V. A plot with similar deviations was previously reported for the corresponding bromides.^{2d} Such deviations are not observed for solvolyses of tosylates I–IV^{2b,c,14b} or for ArCCH₃CF₃OTs¹⁶ and 2-methyl-2-adamantyl chloride.^{2e} These results emphasize the anomalous behavior of solvolyses of *tert*-butyl halides and the need for a revised *Y* scale of solvent ionizing power.

The new Y_{Cl} scale of solvent ionizing power differs significantly from the Winstein–Grunwald *Y* scale. For the range of solvents

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Table IV. Summary of Solvolysis Data for 1-Adamantyl Halides. New Y values for Chlorides (Y_{Cl}) and Bromides (Y_{Br})^a

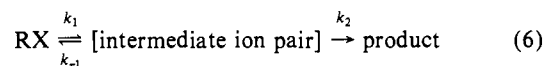
solvent ^b	1-adamantyl-Cl ^c		1-adamantyl-Br ^d	
	$10^6 k, s^{-1}$	Y_{Cl}	$10^6 k, s^{-1}$	Y_{Br}
100% EtOH	0.000 025 ^e	-2.5 ^e	0.001 ^{f,g}	-2.4 ^f
90% EtOH	0.001 ^e	-0.9 ^e	0.04 ^h	-0.84 ^f
80% EtOH	0.008	0.00	0.28	0.00
70% EtOH	0.05	0.8	1.33 ⁱ	0.68 ⁱ
60% EtOH	0.19	1.38	5.1	1.26
50% EtOH	0.83	2.02	21.2	1.88
40% EtOH	4.5	2.75	117	2.62
30% EtOH	27	3.53	698	3.40
20% EtOH	98	4.09	2310	3.92
10% EtOH	200	4.40	4120	4.17
5% EtOH	260	4.51		
H ₂ O	300	4.57	7700	4.44
100% MeOH	0.0005 ^j	-1.2 ^j	0.021 ^k	-1.12 ^k
90% MeOH	0.005 ^j	-0.2 ^j	0.20 ^k	-0.14 ^k
80% MeOH	0.037 ^j	0.67 ^j	1.40 ^{k,l}	0.70 ^k
70% MeOH	0.23	1.46	7.3	1.42
60% MeOH	0.93	2.07	31	2.04
50% MeOH	4.0	2.70	114	2.61
40% MeOH	14.3	3.25	390	3.14
30% MeOH	43.1	3.73	1130	3.61
20% MeOH	101	4.10	2460	3.94
10% MeOH	195	4.39	4100	4.17
80% (CH ₃) ₂ CO	0.0012 ^e	-0.8 ^e	0.06 ^{f,m}	-0.7 ^{f,m}
70% (CH ₃) ₂ CO	0.012 ^e	0.17 ^e	0.50 ^{f,m}	0.2 ^{f,m}
60% (CH ₃) ₂ CO	0.08 ^e	1.00 ^e	3.0	1.03
50% (CH ₃) ₂ CO	0.43	1.73	15.5	1.74
40% (CH ₃) ₂ CO	2.3	2.46	78.0	2.44
30% (CH ₃) ₂ CO	13.1	3.21	362	3.11
20% (CH ₃) ₂ CO	46.9	3.77	1290	3.66
10% (CH ₃) ₂ CO	151	4.28	3150	4.05
5% (CH ₃) ₂ CO	221	4.44		
CH ₃ CO ₂ H	0.0002	-1.6	0.0021	-2.1
HCO ₂ H	12.8	3.20	82.5	2.47
97% CF ₃ CH ₂ OH	5.41	2.83	95	2.53
70% CF ₃ CH ₂ OH	7.34	2.96	171	2.79
50% CF ₃ CH ₂ OH	11.6	3.16	310	3.04
CF ₃ CO ₂ H	300	4.6		
97% (CF ₃) ₂ CHOH	970 ⁿ	5.08	9100	4.51

^a Y Values defined by eq 4 and 5. ^b As in Table I. ^c Kinetic data from Table I unless stated otherwise. ^d Kinetic data from Table II unless stated otherwise. ^e By linear extrapolation of data points from 40–80% ethanol/water and 40 and 50% acetone/water (Figure 1). ^f By linear extrapolation of data points 40, 50, 60, and 80% ethanol/water and 50 and 60% acetone/water in a plot of logarithms of solvolysis rates for 1-adamantyl bromide vs. *tert*-butyl bromide. ^g Literature, $10^{10}k = 8.64$,^{21a} based on an extrapolation using unrealistic activation parameters ($\Delta H^\ddagger = 34.4$ kcal/mol and $\Delta S^\ddagger = +15$ eu). Omission of the 75 °C data gives $\Delta H^\ddagger = 29.7$ kcal/mol, $\Delta S^\ddagger = 3.0$ eu, and k at 25 °C = 5×10^{-9} . ^h Extrapolated value (as described in footnote *f*), $10^6k = 0.03$; literature, $10^6k = 0.047$,^{2e} extrapolated from 50 °C; the average value is quoted. ⁱ Interpolated. ^j By linear extrapolation of data points for 10–70% methanol/water (Figure 1). ^k By linear extrapolation of data points for 10–70% methanol/water in a plot of logarithms of solvolysis rates for 1-adamantyl bromide vs. *tert*-butyl bromide. ^l Literature, $10^6k = 1.53$.⁸ ^m Additional data for *tert*-butyl bromide from ref 12e. ⁿ Reference 2e.

shown in Table IV, Y_{Cl} values span a rate range of $10^{7.5}$, whereas the corresponding Y values span only $10^{5.5}$. Also, the Y_{Cl} values differ substantially from Y values for the less nucleophilic media (carboxylic acids, fluorinated alcohols). The deviations for the less nucleophilic media (Figure 1) are satisfactorily accounted for by eq 2, using previously published N values for solvent nucleophilicity (N_{OTs} and N_{KLi}); see Table V. The choice of N values is not critical, and a scale based on estimated rates of solvolyses of methyl chloride is very similar to the N_{OTs} scale.^{14b} Steric effects on N values should be considered if further refinement of N values were required.^{2d,21b} Nonlinearity of plots for ethanol/water and

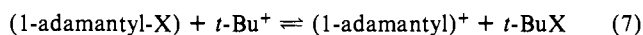
for acetone/water and “dispersion” between various aqueous binary mixtures appear to be due, at least in part, to other anomalies in the solvolyses of *tert*-butyl halides. These small kinetic effects will be discussed elsewhere.

The S_N2 (Intermediate) Mechanism. Solvolyses of *tert*-butyl halides are clearly sensitive to solvent nucleophilicity (l , eq 2, see Table V). We have proposed that nucleophilic solvent assistance occurs during heterolysis of the carbon–leaving group bond via S_N2 (one-stage) or S_N2 (intermediate) mechanisms.² According to this proposal, the 1-adamantyl/*tert*-butyl rate ratios in the weakly nucleophilic, fluorinated media should most closely approach S_N1 behavior. Alternatively, nucleophilic attack could occur on a pre-formed ion-pair intermediate, e.g., as proposed for rate-limiting elimination from *tert*-butyl halides in 97% trifluoroethanol/water.^{7,8} In this mechanism, there is internal return from the contact-ion-pair intermediate ($k_{-1} > k_2$, eq 6), and the



observed rate of reaction (k_{obsd}) is less than the rate constant for ion-pair formation (k_1 , eq 6). The deviations for weakly nucleophilic media (Figure 1) could then be explained by anomalously slow reactions of *tert*-butyl halides. According to this alternative mechanism, the 1-adamantyl/*tert*-butyl rate ratios in the nucleophilic aqueous and alcoholic media should most closely approach simple S_N1 behavior.

Until recently,^{2d} it had been thought for many years that the latter mechanism was correct.^{7,8} In 80% ethanol/water, *tert*-butyl halides react ca. 10^3 times faster than 1-adamantyl halides, as expected from the angle strain involved in forming an sp^2 -hybridized, positively charged carbon atom in the rigid adamantyl framework. This implies that the *tert*-butyl cation should be more stable than the 1-adamantyl cation. However, the equilibrium for anion exchange between 1-adamantyl and *tert*-butyl cations (eq 7) favors the 1-adamantyl cation both in the gas phase and



in solution (Table VI). Apparently the extra β - and γ -carbon atoms provide sufficient stabilization (e.g., by C–C hyperconjugation²³) to overcome any angle strain effects; increasing “bulk” frequently leads to stabilization of ions in the gas phase.²⁴ These and other arguments^{2e} imply that reconsideration of the mechanism of solvolysis of *tert*-butyl halides is required.

S_N1 solvolysis rates parallel carbocation stabilities.²⁵ Therefore the results (Table VI) imply that rates of S_N1 solvolyses of *tert*-butyl halides should be lower than those for 1-adamantyl halides. The observed rate factors are ca. 10^3 times greater in 80% ethanol/water and 30 times greater in water, but only 3 times greater in 97% hexafluoroisopropyl alcohol/water. The solvolytic reactivity predicted from stable ion data (Table VI), 1-adamantyl greater than *tert*-butyl, is closely approached in 97% hexafluoroisopropyl alcohol/water and in trifluoroacetic acid, the least nucleophilic of the solvents examined.^{2b} As solvolyses of 1-adamantyl halides appear to show no mechanistic anomalies (see above), the increase in *tert*-butyl/1-adamantyl rate ratios in the more nucleophilic solvents can be explained by nucleophilic solvent assistance during formation of the *tert*-butyl ion-pair intermediate. Nucleophilic solvent assistance causes charge dispersion, which accounts for the lower m value^{2a} (Table V). Consequently, all of the above experimental data can be accounted for if nucleophilic solvent assistance accompanies heterolysis of the carbon–halogen bond during solvolyses of *tert*-butyl halides. We cannot definitely rule out more complex alternative mechanisms involving “hidden”-ion-pair return during solvolyses of 1-adamantyl halides and both nucleophilic solvent assistance and “hidden” return during solvolyses of *tert*-butyl halides.

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Table V. Correlations of Rate Data for *tert*-Butyl and 1-Adamantyl Halides^a

solvents	eq	chlorides ^b			bromides ^c				
		<i>m</i>	<i>l</i>	std dev in log <i>k</i>	correl coeff	<i>m</i>	<i>l</i>	std dev in log <i>k</i>	correl coeff
5-40% ethanol/water	4, 5	0.67 ± 0.02		0.03	0.999	0.67 ± 0.04		0.05	0.996
50-80% ethanol/water	4, 5	0.83 ± 0.02		0.03	0.999	0.82 ± 0.01		0.02	0.999
10-70% methanol/water	4, 5	0.78 ± 0.01		0.02	0.999	0.77 ± 0.02		0.04	0.999
10-40% acetone/water	4, 5	0.70 ± 0.02		0.02	0.999	0.66 ± 0.01		0.01	0.999
all above solvents	4, 5	0.75 ± 0.01		0.08	0.997	0.71 ± 0.02		0.09	0.994
11 selected ^d	2, <i>N</i> _{OTS} ^e	0.76 ± 0.03	0.30 ± 0.04	0.22	0.994	0.75 ± 0.03	0.33 ± 0.06	0.23	0.993
9 selected ^f	2, <i>N</i> _{KL} ^g	0.82 ± 0.04	0.37 ± 0.11	0.24	0.994	0.82 ± 0.04	0.37 ± 0.10	0.23	0.994
11 selected ^{d,h}	4, 5	0.64 ± 0.06		0.53	0.960	0.66 ± 0.07		0.52	0.961

^a Kinetic data from Table IV and ref 4b, 12c, and 12e. ^b See Figure 1. ^c For a preliminary plot of the earlier data, see ref 2d. ^d As in previous work (ref 2c), the 11 selected solvents are 80% ethanol/water (v/v); 50% ethanol/water (v/v); ethanol, acetic acid, formic acid; trifluoroacetic acid (only for chlorides); methanol; water; 97% trifluoroethanol/water (w/w); 70% trifluoroethanol/water (w/w); 97% hexafluoroisopropyl alcohol/water (w/w). ^e *N*_{OTS} values from ref 2b and 14a and *Y*_{Cl} or *Y*_{Br} values from Table IV. ^f As in footnote d, but excluding trifluoroacetic acid and hexafluoroisopropyl alcohol and with 40% instead of 50% ethanol/water. ^g *N*_{KL} values from ref 22 and *Y*_{Cl} or *Y*_{Br} values from Table IV. ^h Intercepts (ca. 0.3) for eq 4 and 5 are, in effect, second adjustable parameters, whereas for eq 2, *N*_{OTS} the intercept is <0.03—see also discussion in ref 2c.

Table VI. Equilibrium for Anion Exchange between *tert*-Butyl and 1-Adamantyl Cations (eq 7)

anion	"solvent"	Δ <i>G</i> , kcal/mol	reference
Br ⁻	gas phase	ca. -10	10a
Br ⁻	gas phase	≤ -4	10b
H ⁻	AlBr ₃ /CH ₂ Cl ₂	-3.3	11
H ⁻	AlBr ₃ /CH ₂ Br ₂	0	11
H ⁻	theory ^a	-4.1	23

^a Estimated for the gas phase using STO-3G ab initio molecular orbital theory.

For aqueous solvents, the major product of solvolysis of *tert*-butyl halides is the corresponding alcohol (i.e., substitution).²⁶ Therefore, nucleophilic solvent assistance may be described as S_N2 character.^{2d} There is independent evidence for a cationic intermediate in hydrolysis of *tert*-butyl halides; e.g., trapping by nucleophiles including radio-labeled chloride in aqueous acetone under conditions so unfavorable to the S_N2 (one-stage) process that *n*-butyl chloride does not react.²⁷ When this evidence is combined with the evidence for nucleophilic solvent assistance, a clear, specific example of the S_N2 (intermediate) mechanism is apparent. This mechanism has previously been discussed in general terms;^{2c} it involves a nucleophilically solvated ion-pair intermediate (or ion sandwich). The mechanism is similar to a preassociation mechanism²⁸ but with significant nucleophilic solvation (e.g., polarization effect²⁹) stabilizing the ion-pair intermediate. The solvated *tert*-butyl ion-pair intermediate has a low but significant selectivity in trapping by nucleophiles and by solvent,³⁰ suggesting a short but credible lifetime.

Nucleophilic solvation may occur on α-carbon and on β-hydrogen. Both substitution and elimination products are formed during solvolyses of *tert*-butyl halides (even in hexafluoroisopropyl alcohol), and these *might* be formed from a common intermediate. Similar behavior is observed for solvolyses of CF₃(CH₃)₂OSO₂CF₃, but this compound responds more to solvent nucleophilicity and to added nucleophiles; remarkably even in the presence of azide, alkene is the only product detected (>95%, NMR).³¹ These results and others^{2a} clearly show that nucleophilic assistance in tertiary substrates is feasible sterically. For weakly nucleophilically solvent-assisted processes (e.g., *tert*-butyl solvolyses), solvent may be as effective (or more so) than added anionic nucleophiles because encounter and desolvation occur more readily. Anionic

nucleophiles will not provide rate accelerations if the energy gained by nucleophilic stabilization is less than the energy required for desolvation.

Solvent effects on the decomposition of *tert*-butyl halides have recently been analyzed by using the solvatochromic comparison method.³² A wide range of solvents was examined (water, four alcohols, and ten aprotic solvents including pentane), having a range of reactivity so wide (>10¹⁴) that extrapolation errors would be large. Although the solvatochromic results show substantially different emphasis from ours, the main conclusions do not conflict. A solvolysis reaction cannot occur in aprotic solvents, and the decomposition probably occurs via four-center elimination.³³ This process is correlated by the π* scale of solvent dipolarity/polarizability. The solvolysis process in the five protic solvents is correlated by π* and the α scale of hydrogen-bond donor, illustrating the importance of solvation of the leaving group.^{15a} Significantly, the rate constant for trifluoroethanol was excluded from the solvatochromic correlations because it deviated by a factor of 12 from the predicted rate constant.³² Data for acetic acid were not considered, and there were insufficient π* and α values for formic acid, trifluoroacetic acid, and hexafluoroisopropyl alcohols to be included. In the absence of satisfactory correlations for these weakly nucleophilic solvents, the solvatochromic correlations cannot be used to assess the importance of nucleophilic solvent assistance in solvolysis reactions.

The Interpretation of Activation Parameters. By plotting log *k* in our correlations, we relate our studies to Δ*G*[‡]. Much of the data in this series of papers² is relevant to the interpretation of the complex terms Δ*H*[‡], Δ*S*[‡], and Δ*C*_p[‡].^{14c} We do not wish to continue the debate here, but note that the data in Tables I and II include consistent Δ*H*[‡] and Δ*S*[‡] values for hydrolysis of 1-adamantyl halides; our value of Δ*H*[‡] = 22.2 kcal/mol for hydrolysis of 1-adamantyl bromide is significantly lower than the value of 27.88 kcal/mol predicted from solvolyses in *tert*-butanol/water mixtures.³⁴

Conclusions

There is a direct link between carbocation stabilities derived from equilibria between long-lived cations (Table VI) and solvolyses of tertiary substrates in weakly nucleophilic media (e.g., 97% hexafluoroisopropyl alcohol/water). It is predicted that in even less nucleophilic media, 1-adamantyl halides should solvolyze *faster* than *tert*-butyl halides. The latter react relatively more rapidly in nucleophilic media (e.g., water, ethanol) because solvolyses of *tert*-butyl halides are susceptible to nucleophilic solvent assistance during heterolysis of the carbon-halogen bond—S_N2 (intermediate) mechanism. Using new *Y* scales of solvent ionizing power, *Y*_{Cl} and *Y*_{Br}, based on solvolyses of 1-adamantyl halides,

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one can accurately correlate with the $lN + mY$ equation (2) the solvolysis data for *tert*-butyl halides in a wide range of solvents (Table V); the value of l shows the significant sensitivity to solvent nucleophilicity. This establishes quantitatively a link between classical studies on the correlation of solvolysis rates^{4,5} and contemporary studies of stable carbocations (Table VI).

Equations like (2), (4), and (5) should provide useful mechanistic probes of the roles of solvent in many systems, both organic and inorganic. Solvolyses in fluorinated alcohols indicate that the role of solvent as nucleophile in more nucleophilic aqueous or alcoholic solvents has in the past been significantly underestimated.

Experimental Section

Purification of Chemicals. 1-Adamantyl chloride (I, X = Cl) and bromide (I, X = Br; available from Aldrich) were prepared and purified by literature methods.^{8,12a} Trifluoroacetic acid was fractionally distilled through a triple-pass Widmer column. Acetone,⁸ ethanol,^{2a} methanol,⁸ trifluoroethanol,⁷ acetic acid,⁸ and formic acid^{2a} were purified by standard methods.

Kinetic Methods. Stock solutions were checked by studying rates of solvolyses of *tert*-butyl chloride.^{4b} For many solvolyses in aqueous media, the substrate was first dissolved in the organic solvent and solutions were prepared by using matched calibrated pipettes.^{2a} Conductance measurements were made as described previously,^{14c} using CO₂-free solvents for the more dilute solutions (10⁻⁵ M). Titrations of quenched aliquots (ca. 0.005 M) from sealed ampules were carried out on a Radiometer RTS 822 recording titration system fitted with a 2.5-cm³ autoburet, except for the Volhard titrations, carried out on 0.02 M solutions using nitrobenzene to coat the precipitated silver chloride.³⁵

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Registry No. I (X = Cl), 935-56-8; I (X = Br), 768-90-1; *tert*-butyl chloride, 507-20-0.

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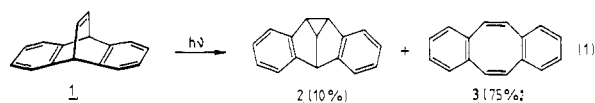
Photochemical and Thermal Denitrogenations of Azoalkanes as Mechanistic Probes for the Diradical Intermediates Involved in the Di- π -methane Rearrangement of Dibenzobarrelene

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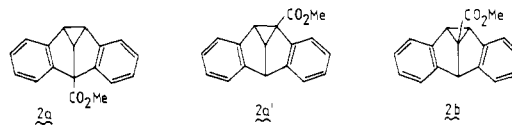
Abstract: The azoalkanes **9** and **10** were prepared from the corresponding urazoles **14** and **15**, which in turn were obtained by reaction of dibenzobarrelene (**1**) with *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD). Thermolysis, direct photolysis at 350 and 254 nm, and benzophenone sensitization lead on denitrogenation respectively to the diradicals **6** and **7**, which are postulated in the di- π -methane rearrangement of dibenzobarrelene (**1**). It is shown that the singlet-state diradicals lead to dibenzobarrelene (**1**) and dibenzocyclooctatetraene (**3**) as minor products and dibenzosemibullvalene (**2**) as major product. Thus, the extent of retro-di- π -methane rearrangement of the diradical **7** derived from azoalkane **10** is small. Formation of benzocyclobutadiene dimer (**4**) via rearrangement of diradical **7** into **8**, a hitherto unrecognized di- π -methane route of dibenzobarrelene (**1**), takes place only to a very small extent in the 254-nm photolysis of azoalkane **10**. The triplet-state diradicals **6** and **7** only afford dibenzosemibullvalene (**2**). The mechanistic implications in reference to the di- π -methane process of dibenzobarrelene are discussed.

The photochemistry of dibenzobarrelene (**1**) has been reported



some time ago¹ to afford dibenzosemibullvalene (**2**) and *sym*-dibenzocyclooctatetraene (**3**). Analogous to related di- π -methane rearrangements,² it was proposed^{1b} that the semibullvalene product **2** was formed via the triplet excited state of **1** and the cyclooctatetraene **3** via its singlet excited state. The regioselectivity of this photorearrangement was tested^{1b} with the 1-carbomethoxy (**1a**) and 7-carbomethoxy (**1b**) derivatives, leading respectively

to the semibullvalenes **2a**, **2a'**, and **2b**. A detailed mechanism



of this di- π -methane rearrangement² is given in Scheme I in terms of the diradical intermediates that might be involved. If one assumes the cyclopropyldicarbonyl diradical **6**, formed by C₃-C₈

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