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Solvolysis of 1-Adamantyl Nitrate. A Y_{ONO_2} Scale and Product Partitioning in Aqueous Ethanol[1]

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The specific rate of solvolysis of 1-adamantyl nitrate has been measured for four solvents over a range of temperature, including 50.0 °C, and for 30 additional solvents at 50.0 °C. Autocatalysis is observed only in 100% 2,2,2-trifluoroethanol, and this can be removed by addition of pyridine. A scale of solvent ionizing power values (Y_{ONO_2}) is developed in terms of the Grunwald–Winstein equation. The Y_{ONO_2} values correlate well with previously determined Y_{OTs} values, with a slope of close to unity. In aqueous ethanol, attack by water is favored. A selectivity value of 1.96 ± 0.04 is observed in the 90–60% ethanol range, falling slightly in value in more aqueous mixtures; possible explanations for this fall are discussed.

Introduction

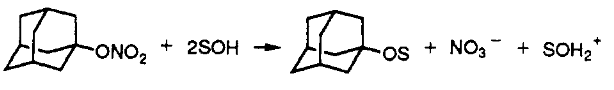
Nitrate esters are usually synthesized either by esterification of the alcohol with nitric acid[2] or by the reaction, under either homogeneous or heterogeneous conditions, of silver nitrate with an alkyl halide.[2,3] The silver salt method has been used to prepare both 1-adamantyl[4,5] and 2-adamantyl[5] nitrates.

There are four pathways known for the reaction of nucleophiles with nitrate esters.[2,6] In addition to the usual nucleophilic attack at carbon and β-elimination, nucleophilic attack at nitrogen and α-elimination (to give a carbonyl compound and nitrite ion) can also occur. The latter two pathways are favored when the attack is by a powerful nucleophile and when there is a relatively strong carbon–oxygen bond in the substrate. For example, benzyl nitrate reacts readily with hydroxide ion to give large amounts of benzaldehyde,[7,8] but in neutral hydrolysis only benzyl alcohol is formed.[8-10] In contrast, neutral hydrolysis of 2-octyl nitrate gave a modest (13%) yield of 2-octanone.[11]

Hydrolyses of tertiary alkyl nitrates proceed at a rate independent of base concentration and yield only alcohols and alkenes.[7,9,12,13] Studies with ^{18}O-enriched water have shown the solvolysis of *tert*-butyl nitrate to proceed with C–O (not N–O) bond cleavage.[13] The solvolyses of nitrate esters, like other esters of strong acids, are not subject to acid catalysis in aqueous media.[9] The decomposition to alkene of *tert*-butyl nitrate in acetonitrile has also been examined and compared with solvolysis.[14]

Nitrate esters have a relatively high solubility in aqueous media, and several have been used by Robertson and coworkers as model compounds for the study of solvolyses in pure water and highly aqueous media.[15,16] For 1-adamantyl nitrate, a very large negative heat capacity of activation ($\Delta C_p^{\ddagger}$) was observed.[5] Such values were originally thought to reflect large degrees of solvent reorganization,[17,18] but it has since been pointed out[15,16,19] that, paralleling a similar consideration of entropy of activation values,[14] they could also be a consequence of extensive ion-pair return. In aqueous–ethanol mixtures, Grunwald–Winstein *m* values[20] of 1.22 and 1.09 were obtained, respectively, for 1- and 2-adamantyl nitrate solvolyses.[21] Further, a correlation between the *m* values in aqueous–ethanol mixtures and the $\Delta C_p^{\ddagger}$ values for hydrolyses in water was reported for a series of nitrate esters, consisting of benzyl and adamantyl nitrates.[21]

In this paper, we present a study of the solvolyses of 1-adamantyl nitrate (eq 1) in four solvents as a function of temperature and in 30 additional solvents only at 50.0 °C. We confirm the Grunwald–Winstein *m* value of close to unity,[21] consistent with the rate-determining step involving an ionization process with C–O bond fission. In the earlier study in pure water, a very accurate value for the specific rate of hydrolysis in pure water at 50.0 °C was reported.[5] In combination, with the 34 values of the present study, this allows *Y* values,[22] in this case for the nitrate ion leaving group (Y_{ONO_2}), to be directly obtained over the full composition range of several aqueous–organic solvents.



(1)

Results

Solvolyses at Various Temperatures. Specific rates of solvolysis were obtained at four temperatures in ethanol, methanol, 80% ethanol, and 2,2,2-trifluoroethanol (TFE). In the first three solvents, constant integrated first-order rate coefficients were obtained. Averages of all of the integrated values from duplicate runs are reported in Table I, together with the enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) of activation.

For solvolysis in TFE, it was found that the integrated first-order rate coefficients rose with extent of reaction;

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Table I. Specific Rates of Solvolysis[a] (k) of 0.0055 M 1-Adamantyl Nitrate at Various Temperatures and Enthalpies ($\Delta H^{\ddagger}$, kcal mol^{-1}) and Entropies ($\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}) of Activation[b]

	10^6k, s^{-1}			
T, °C	EtOH	MeOH	80% EtOH[c]	TFE[d]
16.1				91.2 ± 0.8
25.0				287 ± 2
35.0		0.472 ± 0.003	6.14 ± 0.14[e]	816 ± 11
42.5	0.127 ± 0.003	1.42 ± 0.03		
50.0	0.393 ± 0.016	4.32 ± 0.09[f]	42.0 ± 0.8	3010 ± 40[g]
60.1	1.64 ± 0.03	15.8 ± 0.3	140 ± 2	
70.0	5.99 ± 0.04		420 ± 5	
$\Delta H^{\ddagger}_{323}$	29.5 ± 0.1	27.9 ± 0.1	25.1 ± 0.1	22.1 ± 1.5
$\Delta S^{\ddagger}_{323}$	+3.4 ± 0.5	+3.1 ± 0.3	−1.2 ± 0.5	−0.5 ± 4.8

[a] With associated standard deviations. [b] With associated standard errors. [c] 80 vol of EtOH and 20 vol of H_2O at 25.0 °C. [d] Initial values. [e] At 35.4 °C. [f] At 50.3 °C. [g] In the presence of 0.0055 M pyridine a constant value, averaged throughout duplicate runs, of 3680 (±80) × 10^{-6} s^{-1} was obtained.

Table II. Illustrative Run[a] for the Solvolysis of 0.0054 M 1-Adamantyl Nitrate in 2,2,2-Trifluoroethanol at 50.0 °C

time, min	V_t, mL	V_t/V_∞	10^3k,[b] s^{-1}
0.41	0.930	0.168	3.31
0.83	1.330	0.240	3.46
1.22	1.730	0.313	3.72
1.66	2.130	0.385	3.85
2.11	2.540	0.459	4.05
3.17	3.350	0.606	4.35

[a] 5-mL portions; titrant, 4.80 × 10^{-3} N NaOMe in MeOH; V_0 = 0.540 mL; V_∞ = 5.530 mL. [b] A plot of k against V_t/V_∞ gives an intercept, at V_t/V_∞ = 0, of 2.97 (±0.04) × 10^{-3} s^{-1} (correlation coefficient of 0.996), as opposed to an average k value of 3.79 (±0.35) × 10^{-3} s^{-1}.

Table III. Specific Rates of Solvolysis of 1-Adamantyl Nitrate[a] (k) in Organic and Aqueous–Organic Solvents, at 50.0 °C, and Y_{ONO_2} Values

solvent[b,c]	10^6k,[d] s^{-1}	Y_{ONO_2}[e]
100% EtOH	0.393 ± 0.016[f]	−2.029
90% EtOH	6.48 ± 0.16	−0.812
80% EtOH	42.0 ± 0.8[f]	0.000
70% EtOH	174 ± 4	0.616
60% EtOH[g]	633 ± 1	1.177
50% EtOH[g]	2040 ± 70	1.685
40% EtOH[g]	7730 ± 190	2.264
100% H_2O	631000[h]	4.177
100% MeOH	4.19 ± 0.09[f,i]	−1.001
90% MeOH	29.4 ± 0.8	−0.156
80% MeOH	150 ± 2	0.553
70% MeOH	648 ± 20	1.188
60% MeOH[g]	2610 ± 120	1.793
50% MeOH	9260 ± 580	2.342
90% acetone	0.922 ± 0.016	−1.659
80% acetone	11.1 ± 0.2	−0.577
70% acetone	64.6 ± 0.8	0.186
60% acetone[f,j]	282 ± 3	0.826
50% acetone[f,j]	1240 ± 10	1.470
40% acetone[f,j]	4580 ± 210	2.038
30% acetone[g]	17900 ± 600	2.628
90% dioxane	0.221 ± 0.003	−2.280
80% dioxane	4.06 ± 0.13	−1.015
70% dioxane	29.8 ± 1.0	−0.149
60% dioxane	178 ± 2	0.626
50% dioxane[f,j]	892 ± 17	1.326
40% dioxane[f,j]	4310 ± 110	2.011
100% TFE[k]	3010 ± 40[f]	1.856
97% TFE	3130 ± 130	1.872
90% TFE	3680 ± 140	1.942
80% TFE	4740 ± 300	2.052
80% T–20% E	531 ± 7	1.101
60% T–40% E	68.1 ± 0.7	0.209
40% T–60% E	10.4 ± 0.2	−0.607
20% T–80% E	1.83 ± 0.05	−1.361

[a] Concentration ca. 0.0055 M unless otherwise noted. [b] With water as other component, except for TFE–EtOH (T–E) mixtures. [c] On a volume–volume basis, at 25 °C, except for TFE–H_2O mixtures which are on a weight–weight basis. [d] With associated standard deviations. [e] Logarithm (base 10) of the ratio of the specific rate in solvent under consideration relative to the specific rate in 80% ethanol. [f] From Table I. [g] Concentration of 0.0045 M. [h] From ref 5. [i] Adjusted from value at 50.3 °C, using the activation parameters. [j] Concentration of 0.0035 M. [k] 2,2,2-trifluoroethanol.

an illustrative run is presented in Table II. That the rise in the values was due to an autocatalysis by developing acid was supported by the observation, at the one temperature that was checked, of a constant value throughout the reaction in the presence of an equimolar amount of pyridine. The averages of the initial values from duplicate runs, obtained from plots of integrated first-order rate coefficients against extent of reaction, are reported within Table I, together with the associated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values; within experimental error, these plots were linear.

A value in 80% ethanol at 48.1 °C of 3.55 × 10^{-5} s^{-1} has been reported previously.[21] From interpolation within a plot of log (k/T) against T^{-1}, we obtain a slightly lower value of 3.25 × 10^{-5} s^{-1}.

Solvolysis in Solvents of Varying Ionizing Power. With inclusion of values recorded at 50.0 °C for the four solvents studied at various temperatures, the following solvent systems have been studied at 50.0 °C; 100–40% ethanol (seven compositions), 100–50% methanol (six compositions), 90–30% acetone (seven compositions), 90–40% dioxane (six compositions), 100–80% TFE (four compositions), and a full range of TFE–ethanol mixtures (six compositions). With the already mentioned exception of the solvolysis in pure TFE, constant integrated first-order rate coefficients were obtained throughout each run, and the averages of duplicate determinations are reported in Table III. Also reported in Table III are solvent ionizing power values[20] (Y_{ONO_2}), based on 1-adamantyl nitrate as the standard substrate. The specific rates can be compared, in some instances, with those previously determined[23] for 1-adamantyl iodide at the same temperature.

The titration method previously used to follow the production of strong mineral acids during acetolysis[24] and formolysis[25] could not be used, because nitric acid does not behave as a strong acid in acetic acid;[26,27] the carboxylic acid solvents were excluded from the study.

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Table IV. Distribution of Products[a] from the Solvolysis of 0.0057 M 1-Adamantyl Nitrate in Aqueous Ethanol Mixtures, at 50.0 °C, and Selectivity Values (*S*)[b]

% EtOH[c]	% 1-AdOH[d]	[1-AdOH]/[1-AdOEt][e]	*S*
100	4.0 ± 0.2		
90[f]	43.4 ± 0.6	0.696	1.94 ± 0.05
80	62.5 ± 1.1	1.56	1.94 ± 0.09
70	74.5 ± 2.2	2.76	2.01 ± 0.22
60	81.3 ± 0.9	4.13	1.92 ± 0.11
50	85.2 ± 0.8	5.48	1.71 ± 0.09
40	87.9 ± 0.4	6.93	1.43 ± 0.05

[a] Only 1-adamantanol and 1-adamantyl ethyl ether detected. [b] Ratio of second-order rate coefficients for reaction of intermediate ionic species with water or ethanol; see eq 2. [c] Prepared on volume–volume basis at 25.0 °C. [d] Molar percentage of 1-adamantanol in product; average of five determinations, with associated standard deviation. [e] Ratio of molar concentrations within the product; the percentage of 1-adamantanol incorporated is after substraction of 4.0 (the percentage observed after solvolysis in 100% ethanol). [f] *In the presence of* 0.0063 *M pyridine,* 43.9 (± 1.6)% of 1-adamantanol was present in the product, corresponding to an *S* value of 1.99 ± 0.13.

Product Studies in Aqueous Ethanol. The distributions of products from the solvolysis of 1-adamantyl nitrate in aqueous–ethanol mixtures (100–40% ethanol; seven compositions) at 50.0 °C were determined quantitatively by response-calibrated GLPC. After reaction for in excess of 10 half-lives, the reaction mixtures were directly analyzed. In all cases, only 1-adamantanol and 1-adamantyl ethyl ether were detected as the products. Control experiments showed the ether to have a molar response 1.207 times that of the alcohol. The percentages of 1-adamantanol and the selectivity values (*S*) are recorded in Table IV. The selectivity (*S*) is defined according to eq 2.[28,29] The recorded values are the averages

$$S = \left(\frac{[\text{1-AdOH}]}{[\text{1-AdOEt}]}\right)\left(\frac{[\text{EtOH}]}{[\text{H}_2\text{O}]}\right) \qquad (2)$$

of five determinations. The product distribution from solvolysis in 90% ethanol was unaffected by the presence of a 10% molar excess of pyridine, indicating the absence of any acid-catalyzed equilibration of the products within the time span of these experiments. The small amount (4.0%) of 1-adamantanol detected after solvolysis in 100% ethanol was deducted from each determined percentage of 1-adamantanol in the mixed solvents before insertion into eq 2. As to whether the selectivity is defined as in eq 2 or as the inverse[28] is arbitrary. However, most product studies of the solvolyses of adamantyl derivatives in aqueous ethanol have employed eq 2.

Equation 2 may be rearranged to the form of a linear equation (if *S* is constant), expressed as eq 3. For a

$$[\text{1-AdOH}]/[\text{1-AdOEt}] = S([\text{H}_2\text{O}]/[\text{EtOH}]) \qquad (3)$$

nonlinear plot, the tangent at any point will have a slope equal to the *S* value for that particular solvent composition.[30] For the region of 90–60% ethanol, a good linear plot was obtained with a slope of 1.95 ± 0.05 (correlation coefficient of 0.999). In the more aqueous region, the plot became curved. The value from the slope is in good agreement with the value of 1.96 ± 0.04 obtained by averaging the individual values (Table IV) in the same concentration region.

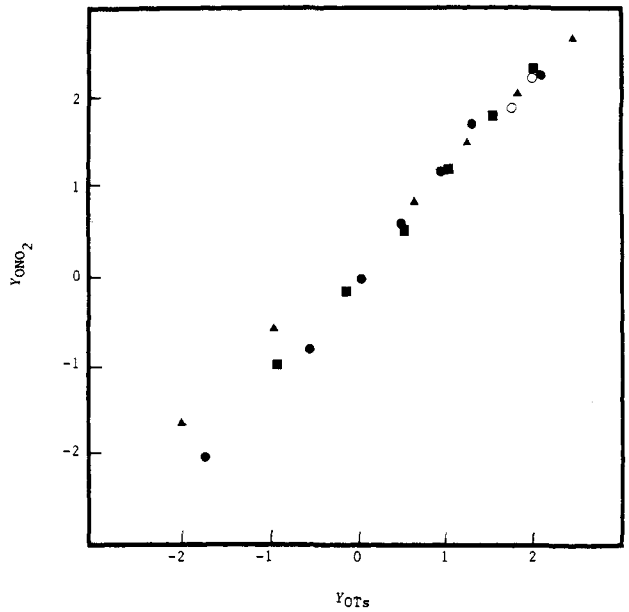

Figure 1. Plot of Y_{ONO_2} against Y_{OTs} for solvolyses in aqueous ethanol (solid circles), aqueous methanol (solid squares), aqueous acetone (solid triangles), and aqueous 2,2,2-trifluoroethanol (open circles).

Discussion

The relatively high solubility of nitrate esters in aqueous–organic solvents high in water content allows the specific rates of solvolysis of 1-adamantyl nitrate to be determined over a wide range of solvent composition. In combination with the very accurate study in pure water by Koshy, Mohanty, and Robertson,[5] a very complete listing of Y_{ONO_2} values is possible for the solvent systems usually employed in Grunwald–Winstein correlations.[22,31] At 50.0 °C, the specific rates of solvolysis measured in this study span a range of almost 5 orders of magnitude: 2.2 × 10^{-7} s^{-1} in 90% dioxane to 1.79 × 10^{-2} s^{-1} in 30% acetone; inclusion of the value in pure water[5] raises the upper level to 63.1 × 10^{-2} s^{-1} and the range to over 6 orders of magnitude.

Autocatalysis was observed only in 100% TFE (Table II). Addition of 3% (by weight) of water is sufficient to remove this effect. These observations are consistent with a previous finding[9] that concentrations of mineral acid of up to 0.1 N had no appreciable effect upon the kinetics of solvolysis of several alkyl nitrates in aqueous ethanol.

The solvolytic reactivity of 1-adamantyl nitrate is comparable to that of 1-adamantyl halides. Indeed, for six solvolyses for which 1-adamantyl iodide data at 50.0 °C were previously reported,[23] the reactivities of the nitrate and the iodide are extremely similar. The ratio of the specific rates of solvolysis of the nitrate relative to the iodide is 1.38 in methanol, 1.67 in 80% methanol, 2.23 in 60% methanol, 1.29 in 80% acetone, 1.58 in 60% acetone, and 1.70 in 40% acetone.

It is rather surprising that nitrate esters and iodides show virtually identical responses to solvent variation; unlike the iodide, the nitrate ion can disperse the developing negative charge over three (oxygen) atoms. The similarity in behavior is shown on a larger scale by the observation that both the 1-adamantyl iodide[23] and the 1-adamantyl nitrate (Table V and Figure 1) give good correlations with Y_{OTs} values,[22,32,33] with slopes of close to

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Table V. Slopes (m) and Intercepts (c) of Plots of Y_{ONO_2} Values against Y Values or Y_{OTs} Values

		Y			Y_{OTs}		
solvent[a]	n	m[b]	c[b]	r[c]	m[b]	c[b]	r[c]
EtOH/H_2O	7	1.02	0.01	1.000	1.17[d]	0.01[e]	0.996
MeOH/H_2O	6	1.08	0.17	1.000	1.14	0.04	1.000
acetone/H_2O	7	0.98	0.10	0.999	0.95	0.25	1.000
dioxane/H_2O	6	1.07	−0.12	1.000	1.16	0.49	1.000
TFE/H_2O	4	0.14	1.70[f]	0.989	1.34[g]	−0.56[h]	0.958
TFE/EtOH	6	1.27	0.55	1.000	1.11	−0.07[f]	0.999
overall	34[i]	1.04[f]	0.13[d]	0.986	1.04[f]	0.14[d]	0.987

[a] For concentration range see Table III. [b] Standard error not greater than ±0.02, unless otherwise indicated. [c] Correlation coefficient. [d] Standard error of ±0.04. [e] Standard error of ±0.05. [f] Standard error of ±0.03. [g] Standard error of ±0.28. [h] Standard error of ±0.52. [i] Two less than sum of n values because both EtOH and TFE are included in TFE–EtOH plus one other data set.

unity. The correlation of the 34 solvent systems studied in this investigation against Y_{OTs} values gives a correlation coefficient of 0.987 and slope and intercept of 1.04 ± 0.03 and 0.14 ± 0.04, respectively. Almost identical values are obtained in a correlation against the original Y scale,[20,22,31] based on *tert*-butyl chloride solvolysis (0.986, 1.04 ± 0.03, and 0.13 ± 0.04). The excellent agreement between the correlations against Y_{OTs} or Y is, however, to some extent fortuitous since the individual mixed solvent systems show larger differences but with no consistent trends, such that the variations just happen to cancel out when all the solvents are considered together (Table V). Although the correlation data for TFE–water mixtures are included in Table V, the values of the specific rates in the four solvent compositions studied are closely bunched together for both 1-adamantyl nitrate and the appropriate standard substrate, and very little significance can be assigned to the values obtained in the correlations using only this subset of solvents. All of the other subsets show slopes close to the value of unity to be expected for an ionization involving carbon–oxygen heterolysis, irrespective of whether plotted against Y or Y_{OTs} values.

The value for m of 1.02 ± 0.01 (at 50.0 °C) in aqueous ethanol is appreciably less than the value of 1.22 reported by Mohanty and Robertson.[21] The range of solvent composition covered is different in the two studies, 100–40% ethanol in the present study and 80–0% ethanol in the earlier study. It can be determined that a linear extrapolation of the 100–40% ethanol data underestimates the experimentally determined specific rate in pure water by a factor of four. Similar, indeed more pronounced, behavior was observed[34] in identical plots against the traditional Y values of the specific rates of solvolysis of 2-adamantyl *p*-toluenesulfonate and other secondary alkyl *p*-toluenesulfonates. In contrast, very little curvature was observed for plots using the corresponding methanesulfonate esters. Since no appreciable change in mechanism would be expected for the modest change in leaving group from *p*-toluenesulfonate to methanesulfonate, the behavior was attributed to solvation effects upon the leaving group at the initial and/or transition state.[34] Presumably, an effect intermediate in character operates in the case of nitrate esters.

Care must be taken in any consideration of small variations in m values for related substrates to ensure not only that identical mixed solvent systems are used but also that the same concentration ranges are employed. Because of the very large heat capacity of activation (ΔC_p^{*}) of −155 ± 9 cal mol^{-1} K^{-1} observed for the hydrolysis of 1-adamantyl nitrate, care must also be taken to minimize the extent of any temperature extrapolations performed in studies of the solvolysis of an adamantyl derivative. Since solvent variation can lead to a reactivity range of greater than 10^5, such extrapolations are frequently difficult to avoid. Even for relatively small linear extrapolations using the Arrhenius or Eyring equations, the frequent curvature of these plots for solvolysis reactions,[35] as indicated by an appreciable ΔC_p^{*} value, will introduce some error. For the extreme case of 1-adamantyl nitrate solvolysis in water, this is clearly indicated by a consideration of the temperature variation of the reported[5] enthalpy (ΔH^{*}) and entropy (ΔS^{*}) of activation values; for a change in temperature from 10 °C to 50 °C, the ΔH^{*} value varies from 28.4 to 21.4 kcal mol^{-1} and the ΔS^{*} value varies from 26.0 to 5.4 cal mol^{-1} K^{-1}. Any linearly extrapolated value for the logarithm of the specific rate at a given temperature will be a function of the temperature range that was actually studied. In the present report, all of the specific rates of solvolysis in the solvent variation study were measured at one temperature (50.0 °C) and extrapolations were avoided.

Bentley has suggested[36] that the correlation of Y_X values against Y_{Cl} values[37] for alcohol–water mixtures can be used for an evaluation of electrostatic effects upon rates of solvolysis. However, for X = Br, I, and OTs, he incorporates values from an earlier publication[23] which are based on studies in a variety of mixed solvent systems, including aqueous acetone. This will lead to a perturbation of the required values for only aqueous–alcohol mixtures; for example, slopes of plots of Y_I against Y_{Cl} have been quoted[23] of 0.90 for EtOH–H_2O, 0.87 for MeOH–H_2O, and 0.79 for acetone–H_2O. Further, some Y_X values are based on studies of the 1-adamantyl derivative and some on studies of the 2-adamantyl derivative. If one considers the two types of scale to be related by eq 4, then, for X =

$$Y_{2\text{-AdX}} = mY_{1\text{-AdX}} + C \qquad (4)$$

methanesulfonate, the m value of 0.982 suggests that only one scale is needed.[22] However, in two other instances where the solvolyses of both isomers have been studied, slopes have been obtained of 0.81,[38] 0.94,[36] or 0.868[39] for X = *p*-toluenesulfonate and of 0.868 for X = 2,2,2-trifluoroethanesulfonate.[40]

We have standardized the way in which the solvent ionizing power ratios for aqueous alcohols are obtained by considering six solvolytic media: 100, 80, 50% ethanol and 100, 80, 60% methanol. Ratios are reported in Table VI

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Table VI. Slopes of Plots of Y_{AdX} against $Y_{\mathrm{1\text{-}AdCl}}$ for Various Leaving Groups in Aqueous Ethanol and Aqueous Methanol Mixtures[a]

X	$Y_{\mathrm{1\text{-}AdX}}/Y_{\mathrm{1\text{-}AdCl}}$	$Y_{\mathrm{2\text{-}AdX}}/Y_{\mathrm{1\text{-}AdCl}}$	$Y_{\mathrm{1\text{-}AdX}}$[b] (est)/$Y_{\mathrm{1\text{-}AdCl}}$
Cl[c]	1.00 (by definition)		
Br[c]	0.96		
I[c]	0.89		
ONO_2[d]	0.83[e]		
$OClO_3$[f]		0.76[g]	0.84[g]
OMs[h]	0.84		
OTs[i]	0.78[j]	0.71	0.78
OTr[k]		0.74	0.82
PFBS[l]		0.66[m]	0.73
OTf[n]		0.69	0.76
Pic[o]	0.49		

[a] Unless otherwise stated, the six solvent compositions (other component water) are 100, 80, 50% EtOH and 100, 80, 60% MeOH. [b] The value for $Y_{\mathrm{1\text{-}AdX}}$ estimated using $Y_{\mathrm{2\text{-}AdX}} = 0.868Y_{\mathrm{1\text{-}AdX}} + 0.027$, (proposed, for X = OTs, in ref 39). [c] 1-AdX data from ref 37. [d] 1-$AdONO_2$ data from this study. [e] 1-$AdONO_2$ data at 50.0 °C. [f] 2-$AdOClO_3$ data from refs 36, 41. [g] At 0.0 °C. [h] Methanesulfonate; data from refs 22, 40, 42. [i] *p*-Toluenesulfonate; 1-AdOTs data from refs 40, 43 and 2-AdOTs data from refs 33, 38. [j] With 90, 60% EtOH and 90% MeOH replacing 80, 60% MeOH. [k] 2,2,2-Trifluoromethanesulfonate; data from ref 33. [l] Pentafluorobenzenesulfonate, data from ref 44. [m] With 90, 70% EtOH and 90% MeOH replacing 50% EtOH and 50% MeOH. [n] Trifluoromethanesulfonate; data from refs 36, 45. [o] Picrate; data from refs 36, 46.

for 11 leaving groups.[22,23,33,36-38,40-46] When the more nucleofugal leaving groups have been studied using the 2-adamantyl ester, the corresponding value involving the 1-adamantyl ester has been estimated using eq 4, incorporating the *m* and *c* values reported[39] from studies of the *p*-toluenesulfonate esters ($m = 0.868$; $c = 0.027$). The Y_X data from the various sources have been conveniently collected together;[22] in the present analyses, care must be taken with the listing of the Y_{OTs} values, since this includes values based on solvolyses of both the 1-adamantyl and the 2-adamantyl esters.

Inspection of the data of Table VI shows that bromide and iodide have ratios only a little lower than the value of 1.00 for the standard compound, 1-adamantyl chloride. The other two purely inorganic leaving groups have values only slightly lower, despite the possibility of extensive internal charge delocalization. Since sensitivities (such as *m* values) usually decrease with increase in temperature,[47] at 25 °C the ratio for nitrate ($Y_{\mathrm{ONO_2}}$ values at 50 °C) will be somewhat higher and the ratio for perchlorate ($Y_{\mathrm{OClO_3}}$ values at 0 °C) somewhat lower than reported. Solvolyses of the five sulfonate esters all give ratios (after correction to $Y_{\mathrm{1\text{-}AdX}}$) in the region of 0.84–0.73. The lower value is a little suspect since it was necessary in the pentafluorobenzenesulfonate analysis to use a slightly different set of solvents; if this value is removed the range narrows to 0.84–0.76. In particular, the *p*-toluenesulfonate and trifluoromethanesulfonate leaving groups, despite a ca. 10^6 difference in nucleofugalities,[40] exhibit virtually identical ratios. The sulfonate anions can be considered as borderline with regard to whether they should be classified as inorganic or organic. The one anion in the listing which would be clearly classified as organic, the picrate, gives a much lower value of 0.49 for the ratio. In a qualitative way, the results can be rationalized by applying the maxim "like dissolves (stabilizes) like" to the influence of the solvent upon the incipient anion of the transition state. As water is replaced by alcohol, the inorganic anions, especially those not capable of internal charge dispersal, will be the most affected (destabilized) by replacing water by ethanol, and the organic anion will be the least affected. Further, those anions, especially chloride,[48] which welcome a strong electrophilic solvent assistance will be handicapped the most as the strong hydrogen bond donor water is replaced by the somewhat weaker ethanol or methanol.[49]

In aqueous ethanol mixtures with up to 60% (by volume) water, the partitioning of the product between water and ethanol has been studied by GLPC (Table IV). In the region of 90–60% ethanol a constant selectivity (*S*) of 1.96 ± 0.04 was observed, indicating a preference for attack by the less nucleophilic water molecules. In more aqueous solvents, the *S* value falls slightly in value. Previous studies of solvolyses in aqueous ethanol of other adamantyl derivatives, possessing either an anionic[29,41,45,50] or a neutral leaving group,[51] have yielded similar results. In contrast, benzhydryl derivatives show a preference for reaction with ethanol, and this preference rises as the ionizing power (water content) of the mixture increases.[52]

For attack on an adamantyl carbocation, it is generally accepted that product formation is at the solvent-separated ion-pair stage and the ultimate product is determined primarily by the identity of the solvent molecule entering to separate the intimate ion pair.[53]

Harris proposed[54] that, for 2-adamantyl arenesulfonates, incorporation of water was favored because it could form two hydrogen bonds to the anion. This cannot be the only factor, however, because adamantyl halides, which can form only one hydrogen bond to the solvent molecule in the solvent-separated ion pair, behave similarly. Recent studies in fluorinated alcohol/water[30,55] and fluorinated alcohol/alcohol[30,55-57] mixtures support the proposal[58] that both the intrinsic electrophilicity (hydrogen bonding ability) and the size of the competing solvent molecules can be important.

Harris pointed out[28] that when more than one species is being attacked, the observed selectivity will be a weighted average of the values for attack on each individual species. For adamantyl derivatives the selectivities *fall* in the more polar (increased water content) aqueous–ethanol mixtures. The fall can be rationalized in terms of, in the more polar mixtures, some of the products being formed from free or almost free ions. Luton and Whiting[50] have remarked that for the solvolysis of tertiary derivatives in highly polar solvents "the involvement of free ions, or of ion pairs so effectively solvated that they approach free cations and anions, is not an absurd suggestion". Benzhydryl derivatives are the classical substrates for dem-

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onstrating retardation by added common ion, indicative of external return.[59] The observation that attack on the benzhydryl cation by the more nucleophilic ethanol molecules is favored[52] would be expected, although the increased preference for attack by ethanol as the water content is increased would suggest that some attack is at an earlier stage[60] (or the nucleophilicities of the two components vary with composition). If, for solvolysis of 1-adamantyl nitrate and related adamantyl derivatives in the higher water content aqueous–ethanol mixtures, some attack is now on free (or almost free) carbocations then this attack would also be expected to favor attack by ethanol. The weighted average of the two processes as measured by a study of the product ratio will be increasingly less in favor of water attack and the observed value for S will fall as the proportion of attack on free carbocations increases.

Experimental Section

Materials. The 1-bromoadamantane (Aldrich, 99%) was recrystallized from hexane. Silver nitrate (Baker, 99.9%) was powdered and dried for 2 h at 130 °C. The 1-adamantyl nitrate was prepared, as previously described,[4,5] by the reaction of the 1-bromoadamantane with the silver nitrate in anhydrous ethyl ether, mp 100.5–102 °C (lit.[4,5] mp 103–103.5 °C, 103–104 °C).

The purification of 2,2,2-trifluoroethanol was using a previously reported procedure.[61] Other solvents were purified as described previously.[43]

Kinetic Procedures. For most kinetic runs, a substrate concentration of ca 5.5×10^{-3} M was used. The solvent under investigation was maintained at the required temperature, and 50 mL were transferred to a flask containing the appropriate amount of solid substrate, which was then tightly stoppered and agitated; for some of the faster runs an ultrasonic bath was used to increase the rate of dissolution.[34,36] After mixing, and a brief period for temperature reequilibration, 5-mL portions were removed at suitable time intervals. For extremely slow runs, 5-mL portions were sealed in glass ampoules, which were then placed in the constant-temperature water bath and removed at appropriate time intervals. For the runs with a specific rate of less than 3×10^{-5} s^{-1}, the interval prior to the infinity determination was reduced by transfer of a 5-mL portion of the reaction mixture to a water bath at a higher temperature.

For runs with a high (>40%) percentage of water, the concentration of substrate was usually reduced and it was initially dissolved in the organic component at 25.0 °C. When the kinetic studies were conducted at higher temperatures, this solution was then equilibrated at the higher temperature and the required volume of water maintained at this temperature (estimated taking into account the relative thermal expansions) added, followed by agitation and reequilibration prior to removing the initial portion.

The portions removed from the reaction mixture (or the contents of the sealed tubes) were quenched by addition to 25 mL of acetone, containing Lacmoid (resorcinol blue) as indicator, cooled within a solid CO_2–acetone slush bath. The previously produced acid was then titrated against a ca. 0.005 M standardized solution of sodium methoxide in methanol.

With the exception of the runs in 100% TFE, in almost all instances the standard deviation from the mean value of all of the integrated first-order rate coefficients from duplicate runs was within 3% of the value. Calculation of the first-order rate coefficients was as previously described.[62]

Product Studies. Analysis of solvolysis products was accomplished by response-calibrated GLPC, using a Packard Model 430 instrument with numerical integration capabilities. An Alltech glass column (61 in. × 2 mm) packed with Carbowax-20M on 80–100-mesh Chromosorb W was used for the separation. Nitrogen was used as the carrier gas.

Solutions of 1-adamantyl nitrate (ca. 0.0057 M) in the appropriate aqueous ethanol solvent (100–40% ethanol) were prepared by transferring 50 mL of the solvent, maintained at 50.0 °C, to a flask containing the substrate. For the slower runs in 100% and 90% ethanol, samples of the reaction mixtures were then sealed in glass ampoules. The experiment in 90% ethanol was performed in duplicate, and in one of the experiments a 10% molar excess of pyridine was added prior to sealing. The 100% ethanol samples were placed in an 85 °C oven for a time corresponding to 10 half-lives at this temperature, and the aqueous–ethanol mixtures were maintained in a 50.0 °C water bath for a time corresponding to at least 10 half-lives. The initiation of the experiments in different aqueous–ethanol mixtures was staggered so that all would be ready for analysis on the same day. Five GLPC determinations were made for each solvent composition studied, and the values were averaged.

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Registry No. 1-Adamantyl nitrate, 32314-61-7.

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