bath was removed, and the stirring was continued for 2 h. During that time the color changed from orange to red. After part of the solvent was evaporated, the precipitated salts were filtered off and the residue was purified by flash chromatography (silica gel, CH_2Cl_2/CCl_4 (1:1)) to yield 70 mg (64%) of **26** as a red solid. Recrystallization from CH_2Cl_2–pentane afforded red to violet crystals: mp 128 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.18 (s, 12 H), 1.30–1.53 (m, 4 H), 1.62–1.78 (m, 4 H), 2.44–2.62 (m, 4 H), 6.95–7.05 (s, 4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.4 (CH_3), 28.4 (CH_2), 35.0 (CH_2), 35.4 (CH_2), 47.8 (C), 129.8 (CH), 140.0 (C), 185.3 (CO), 205.4 (CO); IR ($CDCl_3$) 2962, 2928, 2854, 1724, 1699, 1507, 1470, 1456 cm^{-1}; UV (CH_2Cl_2) (λ_{max} (nm), (log ϵ)) 259 (2.83), 264 (2.84), 272 (2.77), 300 sh, 402 (1.77), 507 (1.62); HRMS (EI, 70 eV) calcd for $C_{21}H_{28}O_3$ ($M^+ - CO$, 1) 328.2094, found 328.2039, calcd for $C_{20}H_{28}O_2$ ($M^+ - 2CO$, 2) 300.2089, found 300.2093, calcd for $C_{19}H_{28}O$ ($M^+ - 3CO$, 5) 272.2140, found 272.2137, calcd for $C_{18}H_{28}$ ($M^+ - 4CO$, 9) 244.2191, found 244.2223, calcd for $C_{17}H_{25}$ ($M^+ - 4CO - CH_3$, 100) 229.1956, found 229.1949. Anal. Calcd for $C_{22}H_{28}O_4$ (356.5): C, 74.13; H, 7.92. Found: C, 73.81; H, 7.92.

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Supplementary Material Available: Tables of bond lengths, bond angles, some torsional angles, and atomic coordinates of **24**, **25b**, and **26** (13 pages). Ordering information is given on any current masthead page.

Multiple Pathways in the Solvolysis of 1-Adamantyl Fluoroformate[†]

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Reactions of 1-adamantyl fluoroformate in hydroxylic solvents have been studied. In solvents of high ionizing power and relatively low nucleophilicity, such as 2,2,2-trifluoroethanol–water mixtures, the reactions parallel those of 1-adamantyl chloroformate, and only solvolysis–decomposition reaction is observed. However, differing from the reactions of the corresponding chloroformate, in other solvents appreciable amounts of attack at acyl carbon occur, more than 90% in ≥80% aqueous ethanol. Entropies of activation for attack at acyl carbon are considerably more negative than for solvolysis–decomposition. For the solvolysis–decomposition, a Grunwald–Winstein m value of 0.70 is observed. The k_{Cl}/k_F ratios for solvolysis–decomposition are in the range of 10^4–10^5, suggesting appreciable C–X bond breaking in the transition state of the rate-determining step and arguing against rate-determining formation of a $1\text{-}Ad^+(OCOX)^-$ ion pair. Attack at acyl carbon is analyzed in terms of the two-term Grunwald–Winstein equation, and sensitivities toward changes in nucleophilicity and ionizing power are identical to those for solvolyses of *n*-octyl fluoroformate, which are believed to proceed via a tetrahedral intermediate. For each of the major pathways, selectivities toward the components of binary hydroxylic solvents are reported and discussed.

Introduction

A recently published study[2] of the solvolysis–decomposition of 1-adamantyl chloroformate (1-AdOCOCl) is extended to 1-adamantyl fluoroformate. Fluoroformates have been studied less extensively than chloroformates,[3,4] and the 1-adamantyl ester is unusual in being commercially available; it is a recommended reagent in peptide synthesis.[5]

Chloroformates have usually been found to undergo attack at acyl carbon, but 1-adamantyl chloroformate gave evidence for this only in ethanol, and even there the percentage of the mixed carbonate formed was less than 1%. In a variety of other solvents commonly used in studies of solvolysis reactions, the only products detected were 1-adamantyl chloride from decomposition and 1-adamantanol and/or 1-adamantyl alkyl ether from a solvolysis process accompanied by a loss of carbon dioxide. This pathway was termed the solvolysis–decomposition pathway.[2] The reaction was formulated as proceeding through a $1\text{-}Ad^+Cl^-$ ion pair, formed either by a concerted process involving expulsion of carbon dioxide or via a very unstable $(1\text{-}AdOCO)^+Cl^-$ ion pair.

For either a concerted or a stepwise pathway, the carbon-halogen bond is broken in the rate-determining step, and considerably reduced rates are to be expected in the solvolysis–decomposition pathway when the chlorine is replaced by fluorine. For an extreme case, the hydrolysis of triphenylmethyl halides in aqueous acetone,[6] the reactivity ratio favors the chloride over the fluoride by as much as 10^6. For bimolecular attack at acyl carbon, it has been found that fluoroformates usually solvolyze slightly faster than chloroformates.[7-9] Accordingly, the net result of replacing chlorine by fluorine should be a pronounced shift away from solvolysis–decomposition and toward bi-

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[†] Dedicated to Professor Michael Hanack on the occasion of his 60th birthday.

[1] On leave from Department of Chemistry, Hanyang University, Sa-dong, Ansan, Kyunggi-do 425-791, Korea, Jan 1988–Feb 1989.

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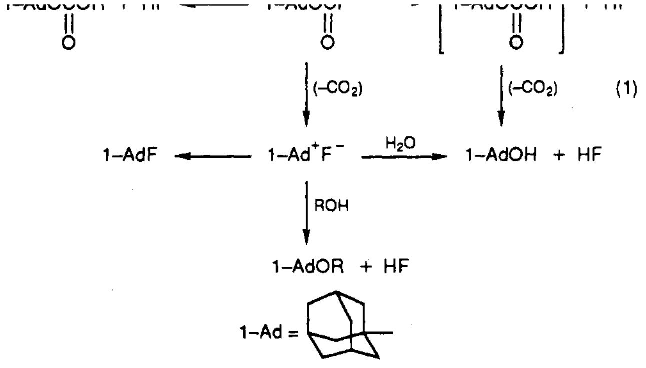
Table I. Percentages of Products in the Solvolysis of 1-Adamantyl Fluoroformate[a] in Aqueous Ethanol and Aqueous Acetone at 50.0 °C[b]

solvent[c]	time (h)	1-AdF (11.97)[d]	1-AdOEt (14.35)[d]	1-AdOH (19.75)[d]	1-AdOCO$_2$Et (33.04)[d]



(1)

Results

Product Studies. Response-calibrated GLPC has been used to determine the products from reaction of 1-AdOCOF at 50.0 °C in aqueous ethanol and aqueous acetone (Table I), aqueous-2,2,2-trifluoroethanol (TFE) (Table II), and TFE–ethanol mixtures (Table III). The small amounts of 1-adamantanol found after reaction in 100% ethanol or in TFE–ethanol mixtures probably result from reaction of the substrate with moisture during manipulation. In the reaction producing 1-adamantyl ethyl carbonate, the reported values are after correction for a 3% conversion of this product to 1-adamantanol during the GLPC analysis.

For reactions in TFE-containing solvents (Tables II and III), the 1-adamantyl fluoride formed by decomposition subsequently undergoes solvolysis. In most instances, the product data obtained after about 10 half-lives for the reaction of 1-adamantyl fluoroformate can be used in conjunction with specific rates of the acid-catalyzed solvolysis of 1-adamantyl fluoride (determined by repeating

Table II. Product Partitioning in the Solvolysis of 1-AdOCOF in Aqueous 2,2,2-Trifluoroethanol (T) at 50.0 °C[a,b]

solvent (% w/w)	1-AdF[c] (11.95)[d]	1-AdOCH$_2$CF$_3$ (14.58)[d]	1-AdOH (19.78)[d]	S (TFE/H$_2$O)

comes 15.0% if extrapolated to time zero. For reactions in 100% and 50% ethanol (Table I), the product ratios were unchanged even when the reaction mixtures stood at 50 °C for well in excess of 10 half-lives. For studies in 80% TFE–20% ethanol and 60% TFE–40% ethanol, the solvolysis rate of 1-adamantyl fluoride was comparable to that of 1-adamantyl fluoroformate and extrapolation, as described above, was not possible.

For reaction in TFE–water mixtures the solvolysis products (as opposed to the decomposition product) are essentially stable. However, for solvolysis in 97% TFE, a small correction is made for a slow conversion of 1-adamantyl ethyl ether to 1-adamantanol. Selectivity values (S) for reaction with TFE relative to water were calculated using eq 2; these values are reported in Table II. For

$$S = \frac{[\text{1-AdOCH}_2\text{CF}_3][\text{H}_2\text{O}]}{[\text{1-AdOH}][\text{TFE}]} \qquad (2)$$

reaction in TFE–ethanol mixtures, only solvolysis–decomposition is observed in 80% TFE–20% ethanol. With larger percentages of ethanol, attack at the acyl carbon becomes of increasing importance. All four solvolysis products (two with and two without concurrent loss of carbon dioxide) are stable under the reaction conditions, and one can calculate selectivities both for solvolysis with loss of carbon dioxide, $S_{\text{S-D}}$ (eq 3), and for solvolysis with retention of carbon dioxide, S_{Acyl} (eq 4). The two series of selectivity values are reported in Table III.

$$S_{\text{S-D}} = \frac{[\text{1-AdOCH}_2\text{CF}_3][\text{EtOH}]}{[\text{1-AdOCH}_2\text{CH}_3][\text{TFE}]} \qquad (3)$$

$$S_{\text{acyl}} = \frac{[\text{1-AdOCO}_2\text{CH}_2\text{CF}_3][\text{EtOH}]}{[\text{1-AdOCO}_2\text{CH}_2\text{CH}_3][\text{TFE}]} \qquad (4)$$

For reaction in aqueous ethanol or aqueous acetone, the situation is more complex because the percentage of 1-adamantanol reported (Table I) arises partially from the solvolysis–decomposition pathway and partially by loss of

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Table III. Product Partitioning in the Solvolysis of 1-AdOCOF in 2,2,2-Trifluoroethanol (T)–Ethanol (E) Mixtures at 50.0 °C[a]

	X in 1-AdX product						
						sensitivity[b] (TFE/EtOH)	
solvent (%v/v)	F (11.92)[c]	OEt (14.33)[c]	OCH_2CF_3 (14.55)[c]	$OCO_2CH_2CF_3$ (22.04)[c]	OCO_2Et (32.69)[c]	S_{S-D}	S_{acyl}
80T–20E[d,e]	(0.03)	(15.5)	(79.4)	0.00	0.00	1.59	
60T–40E[e,f]	(1.36)	(32.1)	(58.1)	0.15	3.19	1.50	0.039
40T–60E	8.6[g]	21.8	14.0	1.04	50.0	1.20	0.039
20T–80E	2.6[h]	12.4[i]	1.5[i]	0.72	79.1		0.045

[a] Difference for sum of each entry from 100% represents 1-AdOH present; values are corrected for 3.0% conversion of $1\text{-AdOCO}_2\text{Et}$ to 1-AdOH during GLPC analysis. [b] Ratio of specific rates for the reaction with 2,2,2-trifluoroethanol or ethanol, respectively. The first entry refers to the solvolysis component of the solvolysis–decomposition (S–D) pathway and the second to the pathway involving attack at the acyl carbon. [c] Retention time (min) under the GLPC conditions. [d] Essentially identical values after 24 and 48 h. [e] Not possible to extrapolate the solvolysis–decomposition values to those in early stages of reaction. [f] After 12 h. [g] Values of 4.8% after 29 days and 3.6% after 42 days; the initial value quoted corresponds to 19% 1-AdF formation within the solvolysis–decomposition products. [h] Values of 2.33% after 37 days and 2.28% after 43 days; the initial value quoted corresponds to 16% 1-AdF formation within the solvolysis–decomposition products. [i] Peaks not separated in integration. Peak area for the minor component estimated from the data for the other solvent compositions by extrapolation of a plot of area for this peak against solvent composition.

Table IV. Specific Rates of Acid-Catalyzed Solvolysis of 1-Adamantyl Fluoride[a] in Aqueous 2,2,2-Trifluoroethanol (T) at 50.0 °C

solvent (%w/w)	[HF][b]	10^6k, s^{-1}
100T	0.0070	350
100T	0.0000	~0.3[c]
97T	0.0069	89
90T	0.0067	7.4 (±0.1)
90T	0.0074	7.5 (±0.3)[d]
90T	0.0136[e]	28
80T	0.0068	1.7
70T	0.0068	~0.6
40T–60E[f]	0.0138[e]	0.25 (±0.01)

[a] Disappearance of the 1-AdF formed was followed (GLPC) after allowing 10 half-lives for reaction of 0.0074 M 1-AdOCOF. [b] Generated by the solvolysis of 1-AdOCOF. [c] Experiment with 0.0079 M 1-AdF (1-AdOH as internal standard) directly dissolved in the solvent. [d] The 1-AdOCOF was allowed to react for 1 day (total solvolysis), and then 0.0042 M 1-AdF was added. [e] From initial [1-AdOCOF] of 0.0144 M. [f] 40% TFE–60% ethanol by volume.

carbon dioxide from the unstable[13] hydrogen carbonate ester formed by attack of water at the acyl carbon. Analysis of this data is deferred until the Discussion.

Kinetics of Reaction of 1-Adamantyl Fluoroformate. The values for the specific rates of reaction of 1-adamantyl fluoroformate, as measured in terms of hydrofluoric acid production, are listed in Table V, and the activation parameters for the seven solvolyses studied at more than one temperature are presented in Table VI.

The calculations of specific rates based on acid development assume that throughout the reaction a constant fraction of the reaction is accompanied by formation of acid. This requirement, previously observed with 1-adamantyl chloroformate,[2] is observed with 1-adamantyl fluoroformate in solvents other than those containing appreciable quantities of fluorinated alcohol. Complications arise in solvents rich in fluorinated alcohol because a moderate rate is observed for the acid-catalyzed solvolysis of the 1-adamantyl fluoride decomposition product (Table IV). However, based on infinity acid titers at about 10 half-lives, constant integrated first-order rate coefficients are observed over appreciable extents of reaction; average values with acceptable standard deviations are reported in Table V. It is fortunate that for most systems studied complications are minimized by only fairly small (<20%) amounts of 1-adamantyl fluoride being produced (eq 1). If the solvolysis of 1-adamantyl fluoride in later stages of reaction was leading to perturbation, one would expect the infinity values to be too high and the integrated values for the specific rate of disappearance of 1-adamantyl fluoroformate to fall as reaction progresses. The only system with appreciable drift in values was the solvolysis in 100% TFE, and here the values rose (approximately linearly; correlation coefficient of 0.970) with extent of reaction, presumably due to autocatalysis by developing hydrofluoric acid,[14] and an initial value was obtained by extrapolation.

Discussion

Comparison with Specific Rates of 1-Adamantyl Chloroformate Solvolysis. For a meaningful comparison of the specific rates of reaction of 1-adamantyl fluoroformate and 1-adamantyl chloroformate, it is important that the comparison is for the same reaction pathway. For nucleophilic attack at acyl carbon, frequently an important component of the overall pathway for 1-adamantyl fluoroformate, we are limited to one observation, 0.67% production of the mixed carbonate in 100% ethanol at 25.0 °C, for 1-adamantyl chloroformate;[2] this corresponds to a specific rate of $0.0067 \times 5.47 \times 10^{-4}$ (3.7×10^{-6}) s^{-1}. Arrhenius extrapolation of the specific rates for reaction of the fluoroformate from higher temperatures (Table V) leads to an overall value at 25.0 °C of 0.229×10^{-6} s^{-1} and, assuming 93% attack at acyl carbon (actually the value at 50 °C), a specific rate for attack at acyl carbon at 25 °C of 0.21×10^{-6} s^{-1} is obtained. The k_{Cl}/k_F ratio is, therefore, 17.6. This value is somewhat higher than values of somewhat below unity previously observed from studies of alkyl haloformates in aqueous acetone[7,8] or ethanol[9] and of *p*-methoxyphenyl haloformates in aqueous dioxane.[8]

The inversion of the ratio could result from the incorporation of a tertiary alkyl group or, contrary to tentative conclusions reached earlier,[2] it could reflect a situation where a major component of the 0.67% 1-adamantyl ethyl carbonate observed in ethanolysis–decomposition of 1-adamantyl chloroformate results not from direct attack on the substrate but from a minor pathway for further reaction of an unstable $(1\text{-AdOCO})^+$ cation involving capture by the solvent. Favoring the explanation in terms of alkyl group variation is the observation[8] that the k_{Cl}/k_F ratio for solvolyses of haloformate esters in 70% aqueous acetone at 30.1 °C increases from methyl (0.14) to ethyl (0.18) or *n*-propyl (0.20) to isopropyl (0.92), suggesting that a

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(14) It has been shown that a given acid has a much greater proton-donating ability toward an added base in pure HFIP than in 97% HFIP: Allard, B.; Casadevall, A.; Casadevall, E.; Largeau, C. *Nouv. J. Chim.* **1980**, *4*, 539.

Table V. Specific Rates of Overall Reaction of 1-Adamantyl Fluoroformate (k) and, for Reaction at 50.0 °C, Division (when Possible) into Components Due to Solvolysis Decomposition (k^{S-D}) and Solvent Attack at Acyl Carbon (k^{Ac})

solvent[a]	T (°C)	10^5k (s^{-1})	%S–D[b]	10^5k^{S-D} (s^{-1})	10^5k^{Ac} (s^{-1})
MeOH	70.0	5.96 ± 0.16			
	60.0	2.96 ± 0.05			
	50.0	1.60 ± 0.02			ca. 1.5
	40.0	0.800 ± 0.010			
EtOH	80.0	2.11 ± 0.05			
	70.0	1.12 ± 0.03			
	60.0	0.529 ± 0.002			
	50.0	0.211 ± 0.003	7.0	0.015	0.196
i-PrOH	70.0	0.117 ± 0.001			
	50.0	0.028 ± 0.001[c]			ca. 0.028
90% MeOH	50.0	11.4 ± 0.1			ca. 11
80% MeOH	50.0	26.2 ± 0.5			
90% EtOH	50.0	3.63 ± 0.05	4.4	0.16	3.47
80% EtOH	60.0	15.9 ± 0.4			
	50.0	7.75 ± 0.12	9.9	0.77	6.98
	40.0	3.92 ± 0.03			
	25.0	1.50 ± 0.02			
70% EtOH	50.0	14.1 ± 0.3	17.9	2.5	11.6
60% EtOH	50.0	25.5 ± 0.7	28.1	7.2	18.3
50% EtOH	50.0	43.7 ± 0.9	44.8	19.6	24.1
70% Me_2CO	50.0	2.21 ± 0.05	*d*		
60% Me_2CO	50.0	7.62 ± 0.11	*d*		
70% Dx[e]	50.0	1.96 ± 0.03			
60% Dx	50.0	7.22 ± 0.12			
50% Dx	50.0	24.6 ± 0.9			
TFE	50.0	61.1 ± 6.7[f]	100	61.1	
97% TFE	50.0	72.9 ± 1.1	100	72.9	
97% TFE	40.0	24.9 ± 0.8			
97% TFE	30.0	7.85 ± 0.08			
97% TFE	20.0	2.30 ± 0.06			
90% TFE	50.0	68.1 ± 0.6	100	68.1	
80% TFE	50.0	80.8 ± 1.7	100	80.8	
70% TFE	50.0	92.3 ± 1.1	100	92.3	
80T–20E[g]	50.0	13.8 ± 0.4	100	13.8	
60T–40E[g]	50.0	2.32 ± 0.08	96	2.23	0.09
40T–60E[g]	50.0	0.626 ± 0.016	46.5	0.29	0.34
20T–80E[g]	50.0	0.456 ± 0.015	17.1	0.078	0.38
97% HFIP	25.0	569 ± 27			
90% HFIP	25.0	100 ± 8			
80% HFIP	50.0	479 ± 19		479[h]	
80% HFIP	25.0	34.8 ± 1.1			
70% HFIP	50.0	303 ± 28		303[h]	
70% HFIP	25.0	26.6 ± 0.6			

[a] On volume–volume basis except for TFE–H_2O and HFIP–H_2O mixtures, which are on a weight–weight basis; [1-AdOCOF] of from 0.003 to 0.015 M (see Experimental Section). [b] From Tables II, III, and VII. [c] Using value for infinity titer from parallel reaction in EtOH. [d] Not possible to partition the overall [1-AdOH] but the ca. 9% 1-AdF (Table I) indicates appreciable amounts of solvolysis–decomposition. [e] Dioxane. [f] Extrapolated initial value; integrated values rise during run, reaching a value of 260 × 10^{-5} s^{-1} at 70% reaction. [g] TFE–EtOH mixtures. [h] Assuming 100% solvolysis–decomposition.

Table VI. Entropies and Enthalpies of Activation for Overall Reaction of 1-Adamantyl Fluoroformate[a]

solvent	$\Delta H^{\ddagger}_{323}$[b] (kcal/mole)	$\Delta S^{\ddagger}_{323}$[b] (eu)
MeOH[c]	13.8 ± 0.4	−38.0 ± 1.3
EtOH[c]	16.8 ± 0.7	−32.7 ± 2.3
80% EtOH[c]	12.6 ± 0.6	−38.5 ± 1.9
i-PrOH[d]	15.1	−41.8
97% TFE[c]	21.7 ± 0.1	−8.0 ± 0.1
80% HFIP[d]	19.4	−9.3
70% HFIP[d]	17.9	−14.7

[a] Using kinetic data from Table V. [b] With associated standard errors. [c] From data at four temperatures. [d] Data at only two temperatures.

value of greater than unity would indeed be observed upon incorporation of a tertiary alkyl group. This trend could possibly be governed by increasing steric effects.

The 1-adamantyl chloroformate reacts almost exclusively by solvolysis–decomposition, and this is also an important pathway in the solvolyses of 1-adamantyl fluoroformate, varying in percentage from essentially 100% in highly ionizing solvents, such as aqueous TFE or aqueous HFIP, to 3% in 95% ethanol. In ethanol at 50 °C, the specific rate of solvolysis–decomposition of 1-adamantyl fluoroformate is 0.015 × 10^{-5} s^{-1} (Table V) and Arrhenius extrapolation of the data for 1-adamantyl chloroformate from lower temperatures[2] leads to a value (after correction for about 0.7% attack at acyl carbon) of 1260 × 10^{-5} s^{-1}. Accordingly, the k_{Cl}/k_F ratio is 8.4 × 10^4, a value 4.8 × 10^3 times greater than that observed for formation of the mixed carbonate by attack at acyl carbon.

For the solvolysis–decomposition pathway in 20%–80% and 40%–60% TFE–ethanol mixtures, the values for 1-adamantyl chloroformate at 25 °C and 1-adamantyl fluoroformate at 50 °C (Table V) give rate ratios of 2.6 × 10^3 and 2.4 × 10^3, respectively. An approximate correction to a common temperature can be made by assuming that the 10-fold decrease in rate of reaction of 1-adamantyl fluoroformate in both 80% and 70% aqueous HFIP as one goes from 50 to 25 °C also applies to solvolysis–decomposition in the TFE–ethanol mixtures. This suggests a k_{Cl}/k_F ratio at 25 °C of roughly 2.5 × 10^4. The lower ratio in TFE–ethanol relative to 100% ethanol probably results from the solvolysis of fluorides being more favored by the electrophilic influence of the relatively acidic TFE than chlorides, fluorides are known to be more susceptible to hydrogen-bonding influences.[15]

The k_{Cl}/k_F ratios of in excess of 10^4, approaching 10^5 in ethanol, are indicative of extensive carbon–halogen bond breaking at the transition state of the rate-determining step. They can be compared with values, for solvolysis in 85% acetone at 25 °C, of 10^5 for *tert*-butyl halides and 10^6 for triphenylmethyl halides.[6] The hydrolysis of *p*-(dimethylamino)benzoyl halides in water at 25 °C leads[16] to a value of 3 × 10^7.

In particular, the ratios of 10^4–10^5 are clearly inconsistent with a rate-determining ionization to a 1-adamantyl–haloformate ion pair; a pathway previously rendered unlikely by comparison[2] of the rates of solvolysis of the chloroformate and the trifluoroacetate.[17] Unfortunately, a value slightly less than maximum values previously observed is not very helpful in distinguishing between a concerted pathway with direct loss of carbon dioxide and a pathway involving loss of carbon dioxide after formation of a $(1\text{-AdOCO})^+F^-$ ion pair.

In the study of 1-adamantyl chloroformate,[2] the extent of decomposition could be estimated from the 20–70% difference between theoretical and measured infinity titers. In the present study, the percentages of 1-adamantyl fluoroformate converted to 1-adamantyl fluoride are considerably lower (0.4–9% in aqueous ethanol and aqueous acetone), and the relatively small differences between theoretical and experimental values will not be highly accurate. For the solvent systems containing TFE, increased amounts of solvolysis–decomposition lead to initially larger amounts of 1-adamantyl fluoride but the values decrease with time due to subsequent acid-catalyzed solvolysis (Table IV). The reported product percentages

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have all been obtained by GLPC.

Acid-Catalyzed Solvolysis. Since fluorine is a better hydrogen-bond acceptor than chlorine, there is the possibility of autocatalysis to the reaction of the fluoroformate by the developing hydrogen fluoride.[15,18-20] Autocatalysis was observed in 100% TFE, the integrated specific rate value having risen about 4-fold at 70% reaction. However, even the 3% water in 97% TFE was sufficient to render the autocatalysis insignificant. This is consistent with the finding that, although acidities are considerably enhanced in fluorinated alcohols, addition of as little as 3% water to HFIP considerably reduces acidities measured within the solvent.[14]

The 1-adamantyl fluoride formed by decomposition of the fluoroformate is subject to solvolysis catalyzed by the acid produced in all the other pathways (Table IV). A control experiment showed that 1-adamantyl fluoride solvolyzed very slowly in 100% TFE at 50 °C but the presence of 7×10^{-3} M hydrogen fluoride led to a rate increase of 3 orders of magnitude. Again, addition of water sharply reduces the acid-catalyzed solvolysis rates; additions of 3% and 10% water led to rate reductions by factors of 4 and 50. In 90% TFE, a doubling of the acid concentration led to an increase in the specific solvolysis rate of 1-adamantyl fluoride of about 4-fold; this more than linear increase in rate with acid concentration is consistent with the finding that acid-catalyzed solvolyses of benzyl fluorides follow the Hammett h_0 function[19] and with the finding that 1-adamantyl fluoride is essentially inert toward 40% hydrofluoric acid but solvolyzes to 1-adamantanol under mild conditions in 65% hydrofluoric acid.[21]

Activation Parameters. For the solvolyses studied kinetically as a function of temperative (Table V), the activation parameters (Table VI) are consistent with a duality of mechanism. In ethanol and 80% ethanol at 50 °C, over 90% of reaction involves attack at acyl carbon (Table V) and the relatively low activation energies and appreciably negative entropies of activation (−33 and −39 eu) are consistent with a bimolecular pathway. It is to be expected that solvolyses in methanol and 2-propanol will also be dominated by bimolecular attack at acyl carbon and entropies of activation of −38 eu and −42 eu are consistent with this prediction. These entropy of activation values are strikingly different to the slightly positive values (3–7 eu) observed[2] for the solvolysis–decomposition reactions of 1-adamantyl chloroformate in the four solvents. The associated standard errors are a little larger than usual for this kind of study; this is probably in large part due to the minor contribution from the solvolysis–decomposition pathway, which is to be expected to have quite different activation parameters.

The reaction in 97% TFE showed no products resulting from attack at acyl carbon (Table II) and, both for this solvent and for 80% and 70% HFIP solvents, essentially pure solvolysis–decomposition reaction is to be expected. For these three solvents, slightly higher activation energies with compensating less negative entropies of activation (−8 to −15 eu) are observed,[22] these values are in the region of the −9 eu observed for solvolysis–decomposition of 1-adamantyl chloroformate in the mixed 90% dioxane solvent.[2]

Selectivity Values from Product Studies. Since no products resulting from attack at acyl carbon were detected in 100–70% TFE–water or in 80% TFE–20% ethanol, it is assumed that these reactions proceed only by solvolysis–decomposition. Small amounts of the two possible mixed carbonates are detected in 60% TFE–40% ethanol, and these become the dominant products with 60% or more ethanol content. The selectivity values, defined according to eq 2 for solvolysis–decomposition in TFE–water, vary from 0.55 to 0.70 as the water content increases to 30% (Table II). The value of 0.63 for 80% TFE is not far removed from the value of 1.03 for 1-adamantyl chloroformate at a 25 °C lower temperature.[2] A value[23] of 1.00 and a value[24] of 0.78 have been reported for the corresponding 1-adamantyl bromide solvolysis at 35 °C.

The stability of all of the solvolysis products in TFE–ethanol mixtures allows direct estimation of selectivity values for the competition between TFE and ethanol both for solvolysis–decomposition and for attack at acyl carbon (Table III). For solvolysis–decomposition, the selectivity values, defined according to eq 3, of 1.6–1.2 are virtually identical to the values for 1-adamantyl chloroformate (at 25 °C) of 1.6–1.1 for the same range of solvent composition. For 1-adamantyl bromide[22-25] and arenesulfonate[26] solvolyses in TFE–ethanol, values in the range of 1.7–1.2 have been reported. For attack at acyl carbon, the selectivity values (eq 4) of 0.039 to 0.045 indicate a preference for reaction with the more nucleophilic[10] ethanol by a factor of about 25. In a study of benzoyl fluoride, believed to react with water by an associative mechanism, determination of the ratio of the two ethers within the product formed from reaction, at 25 °C, in a solvent consisting of 90% water and 10% of a (variable) mixture of ethanol and TFE led[16] to selectivity values for attack by TFE relative to ethanol in the range of 0.16–0.27, favoring ethanol by a factor of 3.7–6.3. Considering the very different reaction conditions, the agreement with the selectivity ratio observed for attack at the acyl carbon of 1-adamantyl fluoroformate is reasonable.

As mentioned briefly in the results section, the 1-adamantyl hydrogen carbonate, produced by attack of water at acyl carbon, rapidly loses carbon dioxide to give 1-adamantanol.[13] For the product studies reported in Table I, the fluoride and ethyl ether result from solvolysis–decomposition, the ethyl carbonate from attack at acyl carbon, and the alcohol from both pathways. For the aqueous acetone systems, there is no simple way of partitioning the 1-adamantanol between the two pathways;[27] the appreciable 9.0 ± 0.3% of 1-adamantyl fluoride does indicate an important contribution from solvolysis–decomposition in the 80–60% acetone range of composition.

In aqueous ethanol, the amount of 1-adamantanol directly accompanying a given amount of 1-adamantyl ethyl ether can be estimated by making use of the observation that the selectivities between ethanol and water for a variety of 1-adamantyl derivatives vary only little with leaving group or temperature.[2,23-26] Further, as discussed earlier in this section, the partitioning between TFE and ethanol is essentially identical for 1-adamantyl fluoro-

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[18] Autocatalysis has been observed in the solvolyses of acyl fluorides: Bevan, C. W. L.; Hudson, R. F. *J. Chem. Soc.* **1953**, 2187.

[19] Swain, C. G.; Spalding, R. E. T. *J. Am. Chem. Soc.* **1960**, *82*, 6104.

[20] Bunton, C. A.; Fendler, J. H. *J. Org. Chem.* **1966**, *31*, 2307.

[21] Stepanov, F. N.; Srebrodol'skii, Yu. I. *J. Org. Chem.* (*USSR*) *Engl. Ed.* **1966**, *2*, 1609.

[22] For a discussion of entropies of activation in unimolecular and bimolecular solvolyses, see: Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, 1969; pp 471–473.

[23] Allard, B.; Casadevall, E. *Nouv. J. Chim.* **1985**, *9*, 725.

[24] Kaspi, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1980**, *102*, 3829.

[25] McManus, S. P.; Zutaut, S. E. *Tetrahedron Lett.* **1984**, *27*, 2859.

[26] Ando, T.; Tsukamoto, S. *Tetrahedron Lett.* **1977**, 2775.

[27] The assignment could be made by oxygen labeling, since the oxygen attached to the adamantyl group is lost in solvolysis–decomposition but retained in the decomposition following an initial water attack at the acyl carbon.

Table VII. Partitioning of 1-Adamantanol Product into Components from Solvolysis–Decomposition (S–D) and Attack at Acyl Carbon and Consideration of Other Product Partitioning Factors

solvent (% EtOH)	[1-AdOH][a] / [1-AdOEt]	1-AdOH via S–D (as % of product)[b]	% of product via S–D[c]	% 1-AdF in S–D products[d]	S_{acyl}[e]
100[f]	0.000	0.00	7.0	12	
95	0.285	0.57	3.0	12	0.57
90	0.575	1.32	4.4	12	0.50
80	1.15	4.4	9.9	15	0.48
70	1.80	9.5	17.9	15	0.47
60	2.54	17.0	28.1	13	0.46
50[f]	3.69	30.5	44.8	11	0.48

[a] These are values obtained previously (ref 2) after solvolysis of 1-AdOCOCl at 25 °C. [b] Percentage of 1-AdOH in overall products predicted to arise from the solvolysis–decomposition pathway; obtained by multiplying the %1-AdOEt (Table I) by the ratio in column 2. [c] Sum of column 3 entry, %1-AdF (Table I), and %1-AdOEt (Table 1), divided by 0.967 (to correct for the 3.3% 1-AdOH observed after solvolysis in 100% EtOH). [d] The % 1-AdF (Table 1) divided first by 0.967 and then divided by the entry in column 4. [e] The % 1-AdOCO$_2$H (which then decomposes to 1-AdOH) is taken as the difference between the measured (Table I) % 1-AdOH (corrected for 3.3% found after reaction in 100% EtOH) and the estimated %1-AdOH from the solvolysis–decomposition pathway (column 3); the selectivity is defined as S = [1-AdOCO$_2$H][EtOH]/[1-AdOCO$_2$Et][H$_2$O]. [f] Mean of the values for the two entries in Table I.

formate at 50 °C and 1-adamantyl chloroformate at 25 °C. It can be assumed, therefore, that the solvolysis product ratios from 1-adamantyl chloroformate in aqueous ethanol at 25 °C can be taken as a good approximation for the corresponding ratios for 1-adamantyl fluoroformate at 50 °C. In this way (Table VII), the total 1-adamantanol product can be partitioned between that formed by solvolysis–decomposition and that formed by attack of water at acyl carbon. In conjunction with the percentage of 1-adamantyl ethyl carbonate formed, this allows calculation of the selectivity for attack at acyl carbon (Table VII). The values obtained for up to 50% water content show remarkably little variation and demonstrate a slight preference, by a factor of about 2, for reaction with ethanol rather than water. For attack at the acyl carbon of p-nitrobenzoyl chloride, selectivity values of 0.9–3.6 have been observed at 25 °C for reaction with ethanol relative to water in 95–50% ethanol.[28-30] In the region of 70–50% ethanol, where we obtain an essentially constant selectivity value of 0.47 ± 0.01, the corresponding identically defined selectivities (k_W/k_E) for p-nitrobenzoyl chloride fall from 0.40 to 0.28.

For benzoyl halides with powerful electron-donating para substituents, the reactions are believed to be S_N1 in character, with capture of the acylium ion at a solvent-separated ion-pair stage; accordingly, the selectivities are similar to those observed[23-26] for adamantyl derivatives. For p-methoxybenzoyl chloride, a value of 1.7–1.3 is observed in aqueous ethanol at 25 °C.[29]

Within the solvolysis–decomposition, the percentage of this pathway involving decomposition to 1-adamantyl fluoride (8–19%) is considerably less than the 20–70% observed[2] for 1-adamantyl chloroformate. This suggests that, at the time of product formation, the halide ions are strongly solvated, such that the chloride ion is more nucleophilic than the fluoride ion. For free or weakly solvated ions, the order of intrinsic nucleophilicities (favoring fluoride ion) is followed.[31] It has been suggested that fluoride ion can especially favor solvolysis because of its efficiency in serving as a general base for attack by solvent.[16]

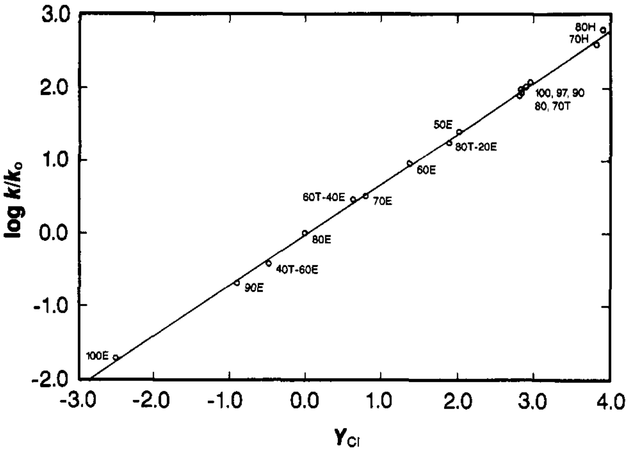

Figure 1. For the component of the specific rate corresponding to the solvolysis–decomposition pathway, a plot of log $(k/k_0)_{\text{1-AdOCOF}}$ (at 50.0 °C) against Y_{Cl} values. The number placed before the code for the solvent refers to the percentage of that solvent, by weight for TFE–H$_2$O and HFIP–H$_2$O mixtures and by volume for all others; any percentage not indicated is water. E represents ethanol, H represents HFIP, and T represents TFE.

Application of the Simple and Extended Grunwald–Winstein Equations. Solvolyses proceeding by ionization, without nucleophilic assistance, follow the simple Grunwald–Winstein equation as the solvent is varied (eq 5). In eq 5, k and k_0 are the specific rates of

$$\log (k/k_0) = mY \tag{5}$$

solvolysis in the solvent under consideration and in 80% ethanol and m is the sensitivity of the solvolysis to changes in solvent ionizing power (Y). The original standard substrate[11] (m value defined as unity) was *tert*-butyl chloride; however, this has been shown to have a small nucleophilic component,[32,33] and scales based on solvolyses of adamantyl derivatives are recommended.[34,35] A scale does not exist for a fluoride ion leaving group (as illustrated in Table IV, the solvolyses of 1-adamantyl fluoride are both slow and subject to strong autocatalysis in weakly basic solvents), and we have used Y_{Cl} values[32,35,36] within the correlations.

The solvolysis–decomposition specific rates are available for 16 solvents for which Y_{Cl} values have been determined; the solvents are indicated within a plot of the correlation (Figure 1). An excellent correlation (correlation coefficient of 0.9994) of log (k/k_0) against Y_{Cl} is obtained with slope of 0.699 ± 0.006 and intercept of −0.022 ± 0.045. With 1-adamantyl chloroformate at a 25 °C lower temperature

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(28) Bentley, T. W.; Harris, H. C. *J. Org. Chem.* **1988**, *53*, 724.

(29) Bentley, T. W.; Koo, I. S. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1385.

(30) Bentley has proposed that selectivities in mixed aqueous organic solvents are best expressed relative to water: Bentley, T. W.; Harris, H. C.; Koo, I. S. *J. Chem. Soc., Perkin Trans. 2* **1988**, 783. Unfortunately, most of the reports of selectivities in aqueous ethanol which are referred to in the present investigation have used the inverse definition. To minimize confusion, we have retained the convention of defining as water relative to ethanol.

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(32) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741.

(33) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635.

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(35) Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121.

(36) Additional Y_{Cl} values have been determined: 90% HFIP (w/w), 4.31; 70% HFIP (w/w), 3.83; 50% HFIP (w/w), 3.80; 60% TFE–40% ethanol (v/v), 0.64; 80% TFE–20% ethanol (v/v), 1.89. D'Souza, M. J.; Kevill, D. N. Unpublished results.

and using the *tert*-butyl chloride Y values (19 solvents), a slope of 0.68 ± 0.03 was obtained.[2] To a rough approximation,[35] for the mainly nonfluorinated alcohols studied, $Y \sim 0.75\ Y_{Cl}$ and a plot of the 1-adamantyl chloroformate data against Y_{Cl} would have a slope of about 0.51. The m_F/m_{Cl} ratio of 1.3 would be slightly higher if the fluoroformate had also been studied at the 25 °C lower temperature used to study the chloroformate. A m value of 1.4 (comparison with 1-adamantyl chloride) for the solvolysis of *p*-(dimethylamino)benzoyl fluoride in aqueous ethanol was considered to arise from a stronger solvation of the incipient fluoride ion in the transition states.[16] The observation of an m_F/m_{Cl} ratio for the haloformate solvolysis–decomposition reactions which is exactly as expected based on this result strongly indicates that this component of the overall 1-adamantyl fluoroformate reaction has been correctly assigned and that an incipient fluoride ion is present in the transition state of the rate-determining step.

Since reactions in TFE–water mixtures are exclusively by solvolysis–decomposition, this is also to be expected for reactions in HFIP–water mixtures: solvents of even higher ionizing power and lower nucleophilicity. A study (Table V) in four solvent compositions at 25.0 °C (97–50% HFIP) gives an excellent Grunwald–Winstein type correlation against Y_{Cl} values[32,36] with a slope of 0.98 ± 0.05 (correlation coefficient of 0.997), consistent with expectation.

For an attack at acyl carbon, solvent nucleophilicity will also be an important consideration and the extended Grunwald–Winstein equation[12] (eq 6) can be used to analyze this type of situation.

$$\log (k/k_0) = lN + mY \qquad (6)$$

In eq 6, the k, k_0, m, and Y are defined as for eq 5 and l represents the sensitivity toward changes in solvent nucleophilicity (N). We have used the recently reported[10] scale of N_T values, based upon solvolysis of the *S*-methyldibenzothiophenium ion. Of the 12 specific rate values available for attack at acyl carbon (Table V), it is unfortunate that, because of the then-observed dominance of solvolysis–decomposition, none are for TFE–water mixtures. Indeed, the range of solvent type, and hence the confidence in the sensitivity values derived, is severely limited by 1-adamantyl fluoroformate reacting essentially completely by solvolysis–decomposition in solvents of low nucleophilicity and fairly high ionizing power. In two of the instances for which specific rates are available, the Y_{Cl} values are unknown; the 10 solvent systems used in the analysis are indicated in Figure 2: a plot of log (k/k_0) against $2.78N_T + 1.01Y_{Cl}$. The best fit l and m values are obtained by multiple regression analysis: l value of 2.78 ± 0.21, m value of 1.01 ± 0.06, and intercept of 0.09 ± 0.16 (correlation coefficient of 0.987).

A study[36,37] of the solvolysis of *n*-octyl fluoroformate at 24.2 °C (in a much wider selection of 21 solvents) led to corresponding values of 1.88 ± 0.15 for l, 0.86 ± 0.08 for m, and intercept of −0.20 ± 0.34 (correlation coefficient of 0.950). However, when the analysis of the *n*-octyl fluoroformate solvolyses is restricted to the same 10 solvents as are available for analysis of the attack at the acyl carbon of the 1-adamantyl ester, the values of 2.71 ± 0.21 for l, 1.03 ± 0.06 for m, and 0.01 ± 0.16 for the intercept (correlation coefficient of 0.987) are virtually identical to those calculated and presented above for solvolytic attack on the 1-adamantyl fluoroformate. This suggests very strongly that attack at the acyl carbon of 1-adamantyl fluoroformate closely parallels the attack on the *n*-octyl ester, which is proposed[37] to proceed by an addition–elimination (tetrahedral intermediate) mechanism.

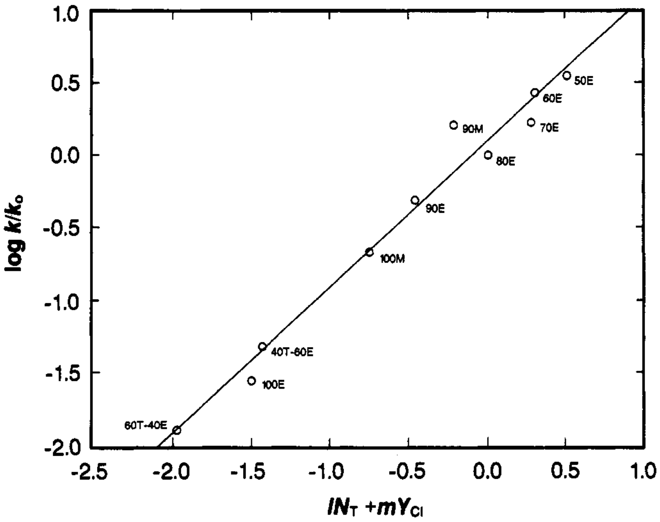

Figure 2. For the attack at acyl carbon, a plot of log $(k/k_0)_{1\text{-AdOCOF}}$ (at 50.0 °C) against $(lN_T + mY_{Cl})$ values, where the best fit values for l (2.78) and m (1.01) are incorporated. M represents methanol; for other information, see the caption for Figure 1.

Summary and Conclusions

Unlike the reactions in hydroxylic solvents of 1-adamantyl chloroformate, where (except for a trace of 1-adamantyl ethyl carbonate in 100% ethanol) only solvolysis–decomposition was observed, the solvolyses of 1-adamantyl fluoroformate have two major reaction pathways: a parallel solvolysis–decomposition pathway and a pathway involving bimolecular attack by solvent at acyl carbon, by what is suggested to be an addition–elimination mechanism.

The solvolysis–decomposition pathway is totally dominant in solvents of high ionizing power and relatively low nucleophilicity, but the contribution from this pathway falls to only 4–10% in 80–100% ethanol. Using dissected rates (at 50 °C), the Grunwald–Winstein m value, for correlations of solvolysis–decomposition specific rates against Y_{Cl} values, of 0.70 is consistent with an ionization mechanism. Probably resulting from a stronger solvation of an incipient fluoride ion, the value is about 30% higher than for 1-adamantyl chloroformate in similar solvents.[2] Additional support for carbon–halogen bond breaking in the transition state, rather than rate-determining ionization to a 1-adamantyl-haloformate ion pair, is given by the observation that under identical conditions the solvolysis–decomposition pathway for fluoroformates proceeds about 10^4–10^5 times slower than that for chloroformates.

Both the m value and the k_{Cl}/k_F ratios are appreciably lower than the corresponding values of 1.4 (in aqueous ethanol) and 3×10^7 (in water) for the S_N1 reactions of *p*-(dimethylamino)benzoyl fluoride,[16] giving some support to the view[38] that a concerted process leading directly to an ion pair and a small stable molecule (in this case carbon dioxide) is involved, rather than loss of halide ion in a S_N1 reaction followed by rapid expulsion of the small stable molecule from the cation.

The selectivities between water and TFE or between TFE and ethanol in the solvolysis component of this

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(38) (a) Conner, J. K.; Maskill, H. *Bull. Chem. Soc. Fr.* 1988, 342. (b) Maskill, H.; Jencks, W. P. *J. Am. Chem. Soc.* 1987, *109*, 2062.

pathway are similar to selectivities that have been observed for 1-adamantyl chloroformate solvolyses[2] and, also, for 1-adamantyl bromide[23-25] and arenesulfonate[26] solvolyses, where the attack by solvent is believed to occur at a solvent-separated ion-pair stage.

A second pathway involves nucleophilic attack at acyl carbon. In ethanol, the only solvent where this pathway was observed for 1-adamantyl chloroformate, a k_{Cl}/k_F ratio of 18 is observed, consistent with a trend of increasing values for solvolyses of alkyl haloformates in 70% acetone[8] as one goes from methyl (0.14), to ethyl (0.18), to isopropyl (0.92). Selectivities favor the more nucleophilic ethanol, by a factor of about 2 in competition with water and of about 25 in competition with TFE. An analysis in terms of the extended Grunwald-Winstein equation gives values for the sensitivities toward nucleophilicity and ionizing power essentially identical to the values recently observed in a study[37] of *n*-octyl fluoroformate in the same solvents: a solvolysis which is believed to proceed by an addition-elimination (tetrahedral intermediate) pathway.

The entropies of activation for reactions believed to involve primarily (>90%) attack at acyl carbon (−33 to −42 eu) are considerably more negative than the values (−8 to −15 eu) for reactions believed to proceed by solvolysis-decomposition. In those solvents (methanol, ethanol, 80% ethanol, and 2-propanol) where attack is predominantly at the acyl carbon, the pathway involved was solvolysis-decomposition for 1-adamantyl chloroformate, leading to entropies of activation which are higher for the chloroformate by an enormous 38–47 eu. This large difference results partially from a change in mechanism and partially from the stronger solvation of the incipient fluoride ion, leading to the ordering of more solvent molecules and a lowering of the entropy of activation.[39]

Experimental Section

Materials. The purifications of 2,2,2-trifluoroethanol,[40] 1,1,1,3,3,3-hexafluoro-2-propanol,[41] and other solvents used[42] were as previously described. The 1-adamantyl fluoroformate (Aldrich) was recrystallized from petroleum ether and stored at 0 °C, mp 32–34 °C (lit.[5] mp 31–32 °C). Small quantities of 1-adamantyl ethyl ether,[42] 1-adamantyl 2,2,2-trifluoroethyl ether,[24] and 1-adamantyl ethyl carbonate,[43] required for calibration purposes, were prepared as previously described. A method for the preparation of 1-adamantyl fluoride[44] was modified slightly by substituting mercuric fluoride for silver fluoride, mp 212–214 °C (lit.[44] mp 210–212 °C dec,[4] lit.[21] mp 260 °C). A small amount of 1-adamantyl 2,2,2-trifluoroethyl carbonate was prepared by substituting 2,2,2-trifluoroethanol for ethanol in the methods used to prepare 1-adamantyl ethyl carbonate.[43] A solution in ethanol of 1-adamantanol (Aldrich, 99%) showed only one solute peak in GLPC, and it was used as received.

Product Studies by GLPC. Solutions, usually containing 0.007–0.008 M 1-adamantyl fluoroformate, in ethanol, aqueous ethanol, aqueous TFE, and TFE–ethanol mixtures were allowed to react at 50 °C for at least 10 half-lives. The products were directly analyzed by response-calibrated GLPC, as previously described.[45] All determinations were carried out at least in duplicate, and an error of ±3% of their value is estimated for the product percentages. For runs in TFE-containing solvents, the experiments were extended so as to obtain product percentages at longer time intervals, and these data were used to calculate specific rates for the acid-catalyzed solvolysis of 1-adamantyl fluoride. Knowledge of these specific rates allowed estimation of the fraction of 1-adamantyl fluoride initially formed from the fluoroformate.

Kinetic Procedures. The rates of production of hydrofluoric acid were followed for solvolyses in several dry alcohols, aqueous–organic mixtures, and TFE–ethanol mixtures. For the aqueous–organic mixtures the solvent composition range was limited by low solubility of the substrate in the more aqueous solvents. The titration technique involved minor modification of one described earlier.[8] Portions were removed at appropriate time intervals and partitioned between 20 mL of pentane and 10 mL of degassed distilled water. The acid previously developed was then titrated against a standardized solution of NaOH in water (ca. 0.005 *M*) to a methyl red–methylene blue endpoint.[46]

Runs in TFE–ethanol solvents and in aqueous–TFE solvents with high TFE content involved removal of 2-mL portions from 25 mL, runs in aqueous–HFIP solvents involved removal of 1-mL aliquots from 10 mL, and runs in other solvents involved removing 5-mL aliquots from 50 mL. The substrate concentration was 0.015 M in solvents rich in TFE or HFIP with reduction to 0.005 M for the more aqueous of the water–TFE and water–HFIP solvents. In other systems, the substrate concentration was usually about 0.007 M, with reduction to 0.003 M for the more aqueous (40–50% water) mixtures. Experimental infinity titers were obtained after at least 10 half-lives and integrated first-order rate coefficients (specific rates) calculated.

Acknowledgment. J.B.K. thanks the Korea Science and Engineering Foundation for support during his participation in this project.

Registry No. 1-AdOCOF, 62087-82-5.

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