Rate and product studies with 2-adamantyl fluoroformate under solvolytic conditions

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ABSTRACT: The specific rates of solvolysis of 2-adamantyl fluoroformate have been measured at 25.0 °C in 20 pure and binary solvents. These are well correlated using the extended Grunwald–Winstein equation, with incorporation of the N_T solvent nucleophilicity scale and the Y_{Cl} solvent ionizing power scale. The sensitivities ($l = 2.15 \pm 0.17$ and $m = 0.95 \pm 0.07$) toward the changes in solvent nucleophilicity and solvent ionizing power, and the k_F/k_{Cl} values are very similar to those previously observed for solvolyses of n-octyl fluoroformate, consistent with the addition step of an addition-elimination pathway being rate-determining. For aqueous ethanol, measurement of the product ratio allowed selectivity values (S) to be determined. The results are compared with those reported earlier for 2-adamantyl chloroformate and mechanistic conclusions are drawn. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: 2-adamantyl fluoroformate; addition–elimination; Grunwald–Winstein equation; product selectivity

INTRODUCTION

A recently published study of the solvolysis-decomposition of 2-adamantyl chloroformate (2-AdOCOCl)[1] is extended to 2-adamantyl fluoroformate (2-AdOCOF). Although the solvolyses of alkyl and aryl haloformates had been extensively studied kinetically, less was known about the kinetics and mechanism of the solvolyses of the above fluoroformate and chloroformate. Accordingly, a study of the reaction mechanism for 2-adamantyl fluoroformate under solvolytic conditions is a subject of continuing interest.

In hydroxylic solvents, chloroformates with a primary alkyl group usually solvolyze with rate-determining attack at the carbonyl carbon. Only in solvents of very low nucleophilicity and very high ionizing power can, in some instances, an ionization pathway be detected.[2–4] Secondary alkyl chloroformates follow the ionization pathway in all but the more nucleophilic and less ionizing solvents (100% and 90% EtOH and MeOH).[1,5] For tertiary alkyl chloroformates,[6] an ionization process, with loss of carbon dioxide, is favored. The ionization pathway with solvolysis-decomposition is the only one operating for solvolyses of 1-adamantyl chloroformate. Loss of carbon dioxide leads to the relatively stable 1-adamantyl cation, which can be captured by simultaneously formed chloride ion or solvent. The corresponding 1-adamantyl fluoroformate[7] showed a very much-reduced tendency toward the ionization and only in solvents of high ionizing power and low nucleophilicity does the behavior parallel to that of the chloroformate. In other solvents, the predominant pathway involves addition–elimination.

The overall picture for solvolyses of primary, secondary and tertiary chloroformates in hydroxylic solvents can be expressed according to Scheme 1, with pathways involving a bimolecular substitution at the acyl carbon shown to the left and pathways involving a rate-determining unimolecular reaction with accompanying loss of carbon dioxide shown to the right.

A recent report concerning the solvolyses of n-octyl fluoroformate and chloroformate[8] found the k_F/k_{Cl} ratio to be only slightly less than unity in 100%EtOH and 100%MeOH and to be somewhat above unity for solvolyses in mixtures of water with ethanol, acetone, dioxane, or 2,2,2-trifluoroethanol (TFE). These ratios were considered to be consistent with the addition step of an addition–elimination mechanism being rate determining.

The extended Grunwald–Winstein equation (Eqn (1))[9–12] has been found to be a very powerful tool for the study of a solvolysis reaction:

$$\log(k/k_o) = lN_T + mY_{Cl} + c \qquad (1)$$

In Eqn (1), k and k_o represent the specific rates of solvolysis in a given solvent and in the standard solvent (80% ethanol), respectively; l is the sensitivity towards

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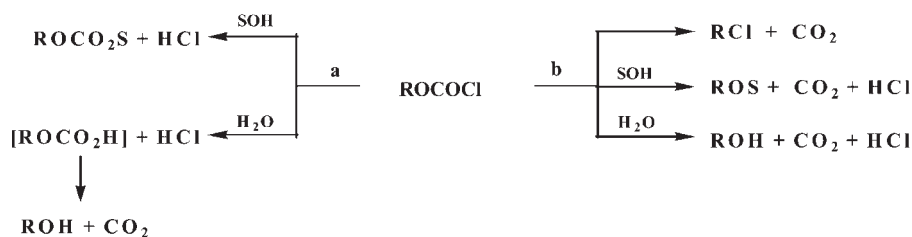
Scheme 1

changes in solvent nucleophilicity (N_T);[11] m is the sensitivity towards changes in solvent ionizing power (Y_{Cl});[12] and c is a constant (residual) term. As the mechanism moves from an ionization pathway to a bimolecular pathway, the l-value should increase and the m-value should decrease. The utility of the Y_{Cl} scale for a process in which nucleophilic attack is accompanied by movement of electron associated with the carbonyl group onto the oxygen of the group has been discussed previously.[8]

RESULTS

The specific rates of solvolysis of 2-adamantyl fluoroformate at 25.0°C are reported in Table 1. The solvents consisted of ethanol, methanol, binary mixtures of water with ethanol, methanol, 2,2,2-trifluoroethanol (TFE), acetone, and three binary mixtures of TFE and ethanol. The N_T and Y_{Cl} values are also reported in Table 1, together with the k_F/k_{Cl} ratios. A determination was also made in methanol-*d* (MeOD).

In methanol, ethanol, and 80% ethanol, specific rates were determined at three additional temperatures, and these values, together with calculated enthalpies and entropies of activation, are reported in Table 2.

For the reactions in ethanol, 90~50% ethanol, and 50% acetone, product studies were carried out using gas chromatography with response-calibrated flame ionization detection, and those results are reported in Table 3.

For the aqueous ethanol, selectivity values (S) were calculated according to Eqn 2,

$$S = \frac{[2-\text{adamantyl ethyl ether}][H_2O]}{[2-\text{adamantano}][EtOH]} \quad (2)$$

In Eqn 2, the product concentrations are divided by the concentration of the component of the solvent producing them. The 5.0% 2-adamantanol observed after reaction in 100% ethanol is deducted from the percentages of this product observed in aqueous ethanol mixtures before calculation of the S values. The selectivity values (S) are presented in Table 3. For comparison, $S_{2\text{-AdOCOCl}}$ values

previously reported[1] for the solvolyses of 2-adamantyl chloroformate are also tabulated.

DISCUSSION

The variance of k_F/k_{Cl} ratios has suggested[14] differences in mechanism and a useful additional probe will be to apply the extended Grunwald–Winstein equation (Eqn 1) and compare the l and m values with those previously

Table 1. Specific rates of solvolysis (with standard deviations) of 2-adamantyl fluoroformate in pure and aqueous solvents at 25.0 °C together with the appropriate solvent nucleophilicity (N_T) and solvent ionizing power (Y_{Cl}) values and the specific rate ratio relative to 2-adamantyl chloroformate (k_f/k_{Cl})

Solvent(%)[a]	$10^5 k$ (s^{-1})	N_T[b]	Y_{Cl}[c]	k_F/k_{Cl}[d]
100 MeOH[e]	2.27 ± 0.09	0.17	-1.17	0.42
90 MeOH	22.1 ± 0.6	-0.01	-0.18	2.40
80 MeOH	41.8 ± 1.0	-0.06	0.67	2.46
70 MeOH	64.9 ± 3.5	-0.40	1.46	2.32
60 MeOH	103 ± 3	-0.54	2.07	1.84
100 EtOH	0.441 ± 0.012	0.37	-2.52	0.37
90 EtOH	8.04 ± 0.07	0.16	-0.94	2.71
80 EtOH	14.9 ± 0.4	0.00	0.00	3.48
70 EtOH	24.4 ± 0.3	-0.20	0.78	3.94
60 EtOH	29.9 ± 0.5	-0.38	1.38	3.01
50 EtOH	38.9 ± 1.0	-0.58	2.02	1.86
80 Me$_2$CO	0.646 ± 0.023	-0.37	-0.83	0.65
70 Me$_2$CO	2.21 ± 0.03	-0.42	0.17	0.82
60 Me$_2$CO	4.28 ± 0.06	-0.52	0.95	0.61
50 Me$_2$CO	11.9 ± 0.2	-0.70	1.73	
70 TFE	0.931 ± 0.03	-1.98	2.96	0.011
50 TFE	3.21 ± 0.2	-1.73	3.16	0.026
60T–40E[f]	0.180 ± 0.02	-0.94	0.63	0.053
40T–60E[f]	0.367 ± 0.02	-0.34	-0.48	0.25
20T–80E[f]	0.425 ± 0.02	0.08	-1.42	0.45

[a] Volume/volume basis at 25.0°C, except for TFE–H$_2$O mixtures, which are on a weight/weight basis.
[b] Values from Ref. 11.
[c] Values from Ref. 12.
[d] Values relative to those for the corresponding solvolysis of 2-adamantyl chloroformate (values from Ref. 1).
[e] Value in 100% MeOD of $1.32(\pm0.10) \times 10^{-5}$ s^{-1}, leading to a k_{MeOH}/k_{MeOD} value of 1.72 ± 0.19.
[f] T–E represents TFE–ethanol mixtures.

Table 2. Specific rates for solvolysis of 2-adamantyl fluoroformate at various temperatures and enthalpies $\Delta H^{\neq}$ (kcal mol^{-1}) and entropies $\Delta S^{\neq}$ (cal mol^{-1}K^{-1}) of activation

Solvent (%)[a]	T (°C)	$10^5 k$ (s^{-1})	$\Delta H^{\neq}_{298.15°C}$[b] (kcal mol^{-1})	$\Delta S^{\neq}_{298.15\,°C}$[b] (cal mol^{-1}K^{-1})
100% MeOH	25.0	2.27 ± 0.09	10.8 ± 0.3	−44.2 ± 1.0
	50.0	10.2 ± 0.9		
	60.0	15.4 ± 0.4		
	70.0	26.9 ± 1.4		
100% EtOH	25.0	0.441 ± 0.013	11.8 ± 0.5	−44.2 ± 2.0
	50.0	2.36 ± 0.05		
	60.0	4.03 ± 0.11		
	70.0	6.09 ± 0.03		
80% EtOH	25.0	14.9 ± 0.4	10.3 ± 0.8	−42.2 ± 3.0
	30.0	20.0 ± 0.4		
	40.0	26.1 ± 0.3		
	50.0	35.2 ± 0.6		

[a] Volume-volume basis at 25.0 °C.
[b] With associated standard error.

obtained for octyl fluoroformate[8] and benzyl fluoroformate.[15]

An analysis using the extended Grunwald–Winstein equation of the data for the specific rates of solvolysis of 2-adamantyl fluoroformate leads to a very good linear correlation with values of 2.15 ± 0.17 for l, 0.95 ± 0.07 for m, −0.06 ± 0.07 for c, and 0.959 for the correlation coefficient (Fig. 1).

The data points for solvolyses in TFE-ethanol mixtures fell below the best fit line, as is often observed in treatments of this type. This phenomenon was very recently discussed[16] and it will not be considered again in this report. Correlations were carried out both with and without the TFE-ethanol data. The results of the correlation are presented in Fig. 1 and reported in Table 4, together with the corresponding parameters obtained in the analyses of earlier studied substrates.

The higher m-values for the solvolyses of fluoroformates, relative to chloroformates, may reflect the need for increased solvation of the developing negative charge on the carbonyl oxygen in the presence of the more electronegative fluorine attached at the carbonyl carbon.

The l/m ratio has been suggested as a useful mechanistic criterion and the values of Table 4 divide nicely into two classes with values of 1.9 to 3.4 for those entries postulated to represent addition–elimination (A–E) and values below 0.84 for those believed to represent ionization (I).

For 2-adamantyl fluoroformate, the value for the ratio l/m of 2.3 is very similar to those previously observed for the solvolyses of benzyl fluoroformate,[15] n-octyl fluoroformate.[8] and benzoyl fluoride,[17] which have been shown to solvolyze with the addition step of an addition–elimination pathway being rate determining.

The consideration of k_F/k_{Cl} ratios in nucleophilic substitution reactions has long been recognized as a useful tool in studying the reaction mechanism.[19] This is especially so when the attack is at an acyl carbon. For S_N1 reaction, a value as low as 10^{-7} was observed in 4-(N,N-dimethylamino)benzoyl halide solvolyses[20] and a low value of 1.3×10^{-4} was also observed for acetyl halide solvolyses in 75% acetone.[19] These values reflect an appreciable ground-state stabilization for the fluoride[21] and the need to break a strong carbon–fluorine bond in the

Table 3. Percentages of the products present after the solvolysis of 2-adamantyl fluoroformate in a binary hydroxylic solvent at 25.0 °C and the calculated selectivity values

Solvent(%)[a]	2-AdOH (18.6)[b]	2-AdOCOOEt (40.1)[b]	$S_{2\text{-AdOCOF}}$[c]	$S_{2\text{-AdOCOCl}}$[d]
100EtOH	5.0	95.0	—	—
90EtOH	25.1	74.9	1.33	1.15
80EtOH	37.9	62.1	1.52	1.20
70EtOH	49.1	50.9	1.59	1.04
60EtOH	57.0	43.0	1.78	0.89
50EtOH	62.2	37.8	2.13	0.56
50Me$_2$CO	100	—	—	—

[a] Volume/volume basis at 25.0 °C,
[b] Retention time (min) under the GC conditions and with a calibration correction factor (C.C.F) for the ester of 0.646.
[c] Selectivity involved in solvent attack at the acyl carbon.
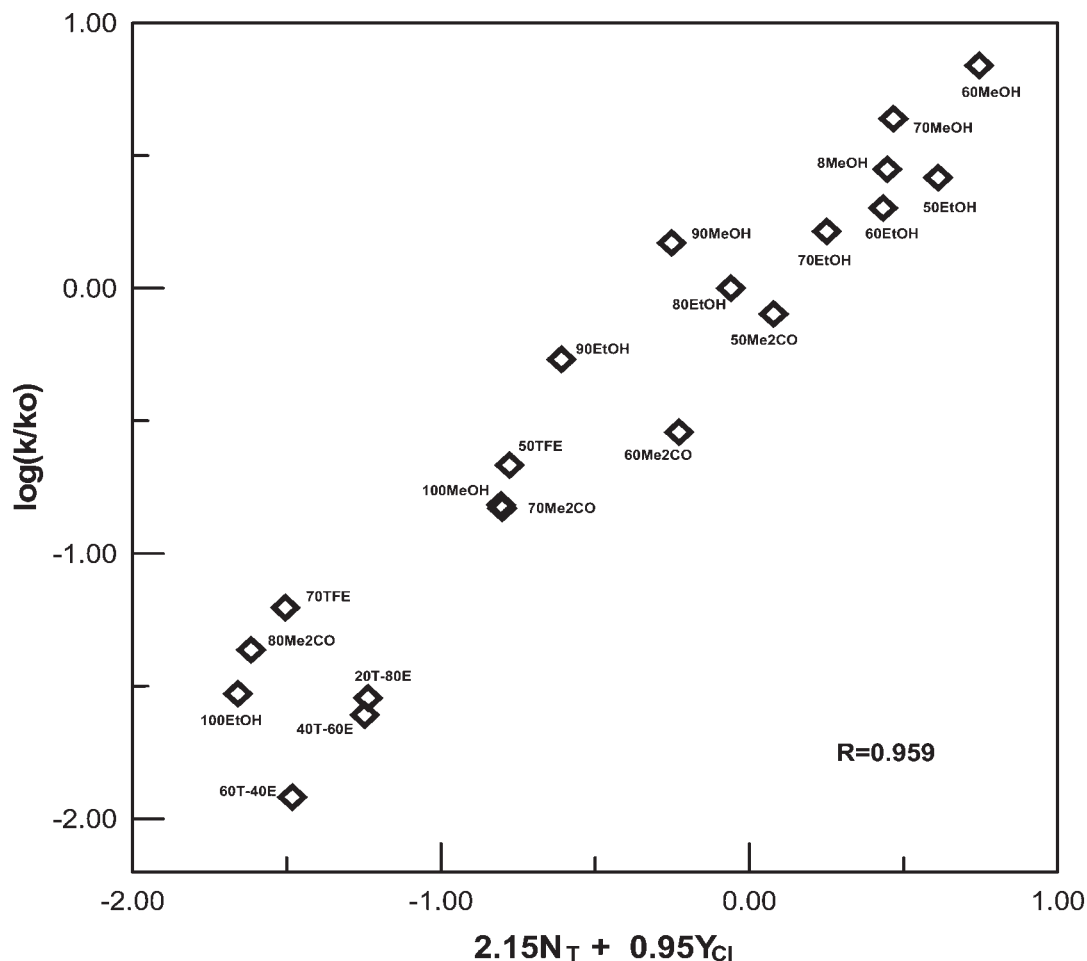[d] Selectivity values for 2-adamantyl chloroformate (Ref. 1).

Figure 1. Plot of log(k/k_o) for solvolyses of 2-adamantyl fluoroformate in pure and binary solvents at 25.0 °C against ($2.15N_T + 0.95Y_{Cl}$)

rate determining step. In contrast, if the addition step is rate-determining, values of close to unity (and frequently above it), reflecting a large electron deficiency at the carbonyl carbon of a haloformate incorporating fluorine,[17] are frequently observed. This situation has recently been discussed in a consideration of *n*-octyl haloformate solvolyses,[8] where k_F/k_{Cl} specific rate ratios of 0.6 to 15 were observed.

Due to the previous study of 2-adamantyl chloroformate[1] involving 19 of the 20 solvent compositions of the present study, a wide range of k_F/k_{Cl} values are available. For a meaningful consideration of the specific rate ratio at 25.0°C (k_F/k_{Cl}) for solvolyses of 2-adamantyl fluoroformate and 2-adamantyl chloroformate (Table 1), it is important that the k_F and k_{Cl} values are for the same reaction pathway. The values for the ratio vary from a low of 0.4 in 100% ethanol (similar to the 0.6 for *n*-octyl haloformates) to a high of 3.9 in 70% ethanol (similar to the 2.9 for *n*-octyl haloformates in 80% acetone). The very low values for 70% TFE, 50% TFE, and 60%TFE-40% ethanol (0.011 to 0.053) are to be expected because of the previously demonstrated[1] dominance of an

ionization pathway for the solvolyses of the chloride in these solvents.

The solvent deuterium isotope effect has previously been studied for several solvolyses of chloroformate esters. In 100% water, the k_{H2O}/k_{D2O} ratio was in the range of 1.8 to 2.0 at 7–25.0°C for a series of substrates believed to react by the bimolecular mechanism. The value for isopropyl chloroformate,[5] in the ionization range, was somewhat lower at 1.25 and the value for diphenylcarbamoyl chloride was lower again at 1.1.[22] More recently, values have become available for the corresponding ratio for methanolysis. Values have been reported for the $k_{MeOH}/k_{MeOD} = 2.1$–2.5 for a series of substituted phenyl chloroformates,[23,24] 2.4 for *p*-nitrobenzyl chloroformate,[13] and 1.88 for 2-adamantyl chloroformate.[1] In the latter value, however, there is probably a contribution from the ionization pathway. The ionization contribution is 12% in ethanol, and this would be expected to increase somewhat in methanol.

The solvent deuterium isotope effect values (Table 1) for methanolysis of 2-adamantyl fluoroformate of $k_{MeOH}/k_{MeOD} = 1.72$ is of a magnitude usually taken to indicate

Table 4. Correlations[a] of the specific rates of the solvolyses by the addition–elimination mechanism for 2-adamantyl fluoroformate and by this mechanism or an ionization mechanism for several other chloroformate and fluoroformate esters, and benzoyl fluoride

Substrate	Mech[b]	n[c]	l[d]	m[d]	c[d]	R[e]	l/m
PhOCOCl[f]	A-E	21	1.68 ± 0.10	0.57 ± 0.06	0.12 ± 0.41	0.973	2.95
MeOCOCl[g]	A-E	19	1.59 ± 0.09	0.58 ± 0.05	0.16 ± 0.17	0.977	2.74
EtOCOCl[h]	A-E	28	1.56 ± 0.09	0.55 ± 0.03	0.19 ± 0.24	0.967	2.84
EtOCOCl[h]	I	7	0.69 ± 0.13	0.82 ± 0.16	-2.40 ± 0.27	0.946	0.84
i-PrOCOCl[i]	I	20	0.28 ± 0.05	0.52 ± 0.03	-0.12 ± 0.05	0.979	0.54
BzOCOCl[j]	A-E	15	1.95 ± 0.16	0.57 ± 0.05	0.16 ± 0.15	0.966	3.42
BzOCOCl[j]	I	11	0.25 ± 0.05	0.66 ± 0.06	-2.05 ± 0.11	0.976	0.38
BzOCOF[k]	A-E	16	1.57 ± 0.20	0.76 ± 0.08	-0.13 ± 0.27	0.933	2.07
BzOCOF[k]	A-E	13	1.43 ± 0.13	0.70 ± 0.05	-0.09 ± 0.17	0.974	2.04
OctOCOF[l]	A-E	23	1.80 ± 0.13	0.79 ± 0.06	0.13 ± 0.34	0.959	2.28
OctOCOF[l]	A-E	19	1.67 ± 0.07	0.76 ± 0.03	-0.08 ± 0.18	0.988	2.20
C_6H_5COF[m]	A-E	41	1.58 ± 0.09	0.82 ± 0.05	-0.09 ± 0.10	0.953	1.93
2-AdOCOCl[n]	I	19	~ 0	0.47 ± 0.03	0.11 ± 0.19	0.970	~ 0
2-AdOCOF[o]	A-E	20	2.15 ± 0.17	0.95 ± 0.07	-0.06 ± 0.07	0.959	2.27
2-AdOCOF[o]	A-E	17	1.92 ± 0.15	0.84 ± 0.06	-0.02 ± 0.06	0.968	2.28

[a] Using Eqn 1.
[b] Addition–elimination (A–E) and ionization (I).
[c] Number of solvent systems included in the correlation.
[d] With associated standard errors, those associated with the c values being the standard errors of the estimate.
[e] Correlation coefficient.
[f] Values from Ref. 18.
[g] Values from Ref. 2.
[h] Values from Ref. 3.
[i] Values from Ref. 5.
[j] Values from Ref. 13.
[k] Values from Ref. 15 and with the second entry omitting the three TFE–ethanol data points.
[l] Values from Ref. 8 and with the second entry omitting the three TFE–ethanol data points.
[m] Values from Ref. 17.
[n] Values from Ref. 1.
[o] This study and with the second entry omitting the three TFE–ethanol data points.

that nucleophilic attack by a methanol molecule is assisted by general–base catalysis by a second methanol molecule.[25,26]

For solvolyses in ethanol, methanol, and 80% ethanol, the values of the enthalpy and the entropy of activation for the solvolysis of 2-adamantyl fluoroformate (Table 2) are 10.3 to 11.8 kcal mol^{-1} and -42.2 to -44.2 cal mol^{-1}K^{-1}, respectively. The very negative entropies of activation are consistent with the bimolecular nature of the proposed rate-determining step.

Product studies were based on determinations by gas chromatography at 10 half lives, estimated from the specific rates of Table 1. The percentage compositions and the selectivity values calculated using Eqn 2 are reported in Table 3. The 5.0% of alcohol after solvolysis in 100% ethanol is similar to the 2.7% found after ethanolysis of 1-adamantyl chloroformate[6] and the 3.3% found after ethanolysis of 1-adamantyl fluoroformate.[7] For the 2-adamantyl chloroformate in 100% ethanol, a smaller amount of 2-adamantanol (1.3%) was found, and since number 2-adamantanol was found for the reaction in 100% TFE, this would appear to be due to the presence of a small concentration of water in the ethanol.[1] As previously proposed,[6,7] this product can also result from the reaction of the substrate with moisture during manipulation. The product studies for the solvolyses of

2-adamantyl fluoroformate (Table 3) are also consistent with an addition–elimination pathway. The products can be rationalized in terms of mixed carbonate esters being formed from reaction with either a pure alcohol or with the alcohol component of a mixed solvent and 2-adamantanol resulting from an initial water attack being followed by carbon dioxide loss from the initially formed hydrogen carbonate (Scheme 1a). In particular, there was no evidence for either 2-adamantyl fluoride, from a competing decomposition, or the appropriate mixed ether, which would have been formed by an ionization pathway involving loss of carbon dioxide, followed by reaction of the carbocation with an alcohol component of the solvent (Scheme 1b).

In aqueous ethanol, the selectivity values (S) increase slightly from a value of 1.33 in 90% ethanol to 2.13 in 50% ethanol (Table 3). These values are not very different to those which have been observed for other solvolyses of carbonyl chlorides and fluorides believed to follow the addition–elimination pathway. Previous S values for attack at the acyl carbon of chloroformate and fluoroformate esters, which are believed to follow an addition–elimination pathway, with the addition step being rate determining, have usually been somewhat larger, with values of 2.0 to 4.1 for benzyl chloroformate in 90%~50%ethanol,[13] 2.2 to 3.6 for benzyl fluoroformate

in 90%~50%ethanol,[15] 4.1 and 6.1 for *p*-nitrobenzyl chloroformate in 80% and 60%ethanol, [13] and 2.6 and 4.6 for *p*-nitrophenyl chloroformate in 80% and 60%ethanol.[27] The lower *S* values for nucleophilic attack at the acyl carbon in the present study and in the study of the corresponding chloride could be a consequence of a higher steric hindrance associated with the 2-adamantyl cage slightly increasing the extent of reaction with the smaller water molecules at the expense of the bulkier ethanol molecules.

The falling of the *S* value to 0.56 for solvolysis in 50% ethanol, previously reported for solvolyses of 2-adamantyl chloroformate,[1] is consistent with the change over to an ionization pathway in all but the more nucleophilic and least ionizing solvents (100% and 90% EtOH and MeOH). In the more aqueous solvents, *S* values for bimolecular reaction of the chloride are not available for comparison.

CONCLUSIONS

The solvolyses of 2-adamantyl fluoroformate give a satisfactory extended Grunwald–Winstein correlation (Eqn 1) over a wide range of N_T and Y_{Cl} values. The sensitivities to changes in N_T and Y_{Cl} ($l = 2.15$ and $m = 0.95$) are very similar to those for several fluoroformate and chloroformate esters (Table 4), which have been shown to solvolyze with the addition step of an addition–elimination pathway being rate determining.

The k_F / k_{Cl} values obtained in a comparison with the corresponding solvolysis of 2-adamantyl chloroformate are similar to those for solvolyses of n-octyl fluoroformate relative to n-octyl chloroformate, consistent with a bimolecular addition–elimination mechanism, proceeding through a tetrahedral intermediate. Favoring the explanation of a relatively low value (when both react by the addition–elimination pathway) in terms of alkyl variation is the observation[28] that the k_F / k_{Cl} ratio for solvolyses of haloformate esters in 70% aqueous acetone at 30.1°C decreases from methyl (7.16), ethyl (5.46) or *n*-propyl (4.95) to isopropyl (1.09), consistent with the value of slightly less than unity for the 2-adamantyl haloformate solvolyses in this solvent (at 25.0°C).

The solvent deuterium isotope effect value for methanolysis, $k_{MeOH} / k_{MeOD} = 1.72$ is of a magnitude usually taken to indicate that nucleophilic attack by a methanol molecule is assisted by general-base catalysis by a second methanol molecule.

The entropies of activation (-42.2 to -44.2 cal mol^{-1}K^{-1}) for 2-adamantyl fluoroformate reaction, believed to involve rate-determining attack at acyl carbon, are considerably more negative than the values for reactions believed to proceed by an ionization pathway (the entropies of activation for 1-adamantyl chloroformate are $+3.3$ to $+6.7$ cal mol^{-1}K^{-1}).

The selectivity values ($S = 1.33$ to 2.13) for solvolyses of 2-adamantyl fluoroformate in 90%–50% aqueous ethanol are slightly lower but similar to those which have been observed for other solvolyses of carbonyl chlorides and fluorides believed to follow the addition–elimination pathway.

In the present study, unlike the solvolyses of 2-adamantyl chloroformate, where, in most solvents, solvolysis-decomposition (ionization pathway) was observed, the solvolyses of 2-adamantyl fluoroformate have a pathway involving bimolecular attack by solvent at acyl carbon, and it is suggested that the addition step of an addition–elimination pathway is rate determining (Scheme 1a).

EXPERIMENTAL

2-Adamantyl fluoroformate (b.p. 118–120 °C/1.2 mmHg) was prepared from 2-adamantyl alcohol via reaction with 1-chloroethyl chloroformate by a procedure as described earlier.[29] Solvents were purified as previously described.[6]

The kinetic procedures were as described earlier,[7,28] using a substrate concentration of about 7.0×10^{-3} M and with 5 ml aliquots removed for titration.

The percentages of products formed during the solvolyses were determined by response-calibrated GLPC, as previously described,[6,7] using a 2.1 m glass column containing 10% Carbowax 20M on Chromosorb WAW 80/100 with an injection temperature of 150 °C and column temperature 100 °C. The retention times (in min) of observed products are reported in Table 3.

REFERENCES

1. Kyong JB, Yoo JS, Kevill DN. *J. Org. Chem.* 2003; **68**: 3425.
2. Kevill DN, Kim JC, Kyong JB. *J. Chem. Res., Synop.* 1999; 150.
3. Kevill DN, D'Souza MJ. *J. Org. Chem.* 1998; **63**: 2120.
4. Kyong JB, Won H, Kevill DN. *Int. J. Mol. Sci.* 2005; **6**: 87.
5. Kyong JB, Kim YG, Kim DK, Kevill DN. *Bull. Korean Chem. Soc.* 2000; **21**: 662.
6. Kevill DN, Kyong JB, Weitl FL. *J. Org. Chem.* 1990; **55**: 4304.
7. Kevill DN, Kyong JB. *J. Org. Chem.* 1992; **57**: 258.
8. Kevill DN, D'Souza MJ. *J. Chem. Soc., Perkin Trans. 2* 2002; 240.
9. Grunwald E, Winstein S. *J. Am. Chem. Soc.* 1948; **70**: 846.
10. Schadt FL, Bentley TW, Schleyer PvR. *J. Am. Chem. Soc.* 1976; **98**: 7667.
11. Kevill DN. In *Advances in Quantitative Structure–Property Relationships*, Vol. **1**. Charton M (ed.). JAI Press: Greenwich, CT, 1996; pp. 81–115.
12. Bentley TW, Llewellyn G. *Prog. Phys. Org. Chem.* 1990; **17**: 121.

13. Kyong JB, Park BC, Kim CB, Kevill DN. *J. Org. Chem.* 2000; **65**: 8051.
14. Kevill DN. In *The Chemistry of the Functional Groups: The Chemistry of Acyl Halides* Patai S (ed.). Wiley: New York, 1972; Chapter 12
15. Kyong JB, Ryu SH, Kevill DN. *Int. J. Mol. Sci.* 2006; **7**: 186.
16. Kevill DN, Miller B. *J. Org. Chem.* 2002; **67**: 7399.
17. Kevill DN, D'Souza MJ. *J. Org. Chem.* 2004; **69**: 7044.
18. Kevill DN, D'Souza MJ. *J. Chem. Soc., Perkin Trans. 2* 1997; 1721.
19. Swain CG, Scott CB. *J. Am. Chem. Soc.* 1953; **75**: 246.
20. Song BD, Jencks WP. *J. Am. Chem. Soc.* 1989; **111**: 8470.
21. (a) Wiberg KB, Hadad CM, Rablen PR, Cioslowski J. *J. Am. Chem. Soc.* 1992; **114**: 8644; (b) Wiberg KB, Rablen PR. *J. Org. Chem.* 1998; **63**: 3722.
22. Kivinen A. In *The Chemistry of Acyl Halides* Patai S (ed.). Interscience: New York, 1972; pp. 198–200.
23. Yew KH, Koh HJ, Lee HW, Lee I. *J. Chem. Soc., Perkin Trans. 2* 1995; 2263.
24. Koo IS, Yang K, Kang K, Lee I. *Bull. Korean Chem. Soc.* 1988; **19**: 968.
25. Ryu ZH, Shin SH, Lee JP, Lim GT, Bentley TW. *J. Chem. Soc., Perkin Trans. 2* 2002; 1283.
26. Oh YH, Jang GG, Lim GT, Ryu ZH. *Bull. Korean Chem. Soc.* 2002; **23**: 1083.
27. Koo IS, Yang K, Kang K, Lee I, Bentley TW. *J. Chem. Soc., Perkin Trans. 2* 1998; 1179.
28. Queen A, Nour TA. *J. Chem. Soc., Perkin Trans. 2* 1976; 935.
29. Dang VA, Olofson RA, Wolf PR, Piteau MD, Senet JPG. *J. Org. Chem.* 1990; **55**: 1847.