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Solvolysis−Decomposition of 2-Adamantyl Chloroformate: Evidence for Two Reaction Pathways

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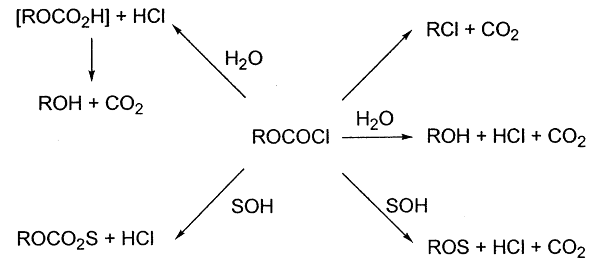
Reaction of 2-adamantyl chloroformate under a variety of solvolytic conditions leads to 2-adamantyl chloride accompanied by solvolysis products, some with and some without retention of the CO_2 unit. For example, in 100% ethanol, only 4.8% 2-adamantyl chloride is formed with the mixed carbonate (88%) being the dominant product, and in 100% 2,2,2-trifluoroethanol, the products are both formed with loss of CO_2, 59% of the chloride and 41% of the ether. With exclusion of the specific rates in 100% and 90% ethanol and methanol, a good Grunwald−Winstein plot against Y_{Cl} values (solvent ionizing power) is obtained, with a slope of 0.47 ± 0.03. The results are compared with those reported earlier for 1-adamantyl chloroformate and isopropyl chloroformate and mechanistic conclusions are drawn.

The solvolyses of methyl,[1] primary,[2,3] and aryl[4] chloroformates proceed predominantly by an addition−elimination pathway, with the addition step being rate-determining. Only in solvents of very low nucleophilicity and very high ionizing power can, in some instances, an ionization pathway be detected. For benzyl[5] (but not the *p*-nitro derivative) and isopropyl[6] chloroformates, there is a delicately balanced solvent-determined duality of mechanism operative. For the reaction of benzyl chloroformate under solvolytic conditions in aqueous 2,2,2-trifluoroethanol (TFE) containing at least 90% TFE, decomposition can accompany the solvolysis with formation of 37%−48% benzyl chloride. The overall picture can be expressed as in Scheme 1, with pathways involving substitution at the acyl carbon (bimolecular or unimolecular) shown to the left and pathways involving loss of carbon dioxide accompanying the substitution to the right. In some instances, such as for the reaction of isopropyl chloroformate, the pathway involving the loss of carbon dioxide can also exhibit an elimination component, leading to alkene.

SCHEME 1



In the solvolysis−decomposition of the tertiary 1-adamantyl chloroformate,[7] only in ethanol was a trace of a product with retention of CO_2 observed, and the kinetics and products could be interpreted in terms of solvolysis−decomposition, proceeding through the relatively stable 1-adamantyl cation. The corresponding 1-adamantyl fluoroformate showed a very much reduced tendency toward ionization and only in highly ionizing solvents of low nucleophilicity does the behavior parallel the chloroformate.[8] In other solvents, the predominant pathway involves addition−elimination. The lower reactivity of 1-AdOCOF under ionization conditions strongly suggests that the initial ionization is not to $1\text{-Ad}^+(\text{OCOX})^-$. Also, the much faster reaction of 1-adamantyl fluoroformate relative to 1-adamantyl trifluoroacetate, despite the similar electron-withdrawing abilities of fluorine and trifluoromethyl,[9] supports this viewpoint.[8] The plausible pathways, with indication of the ion pairs involved, are shown in Scheme 2.

This report presents the results of a study concerning the kinetics and product distribution for reactions of 2-adamantyl chloroformate under solvolytic conditions. Comparisons with the corresponding reactions of isopropyl chloroformate (secondary but acyclic) and 1-adamantyl chloroformate (cage structure but tertiary) allows a

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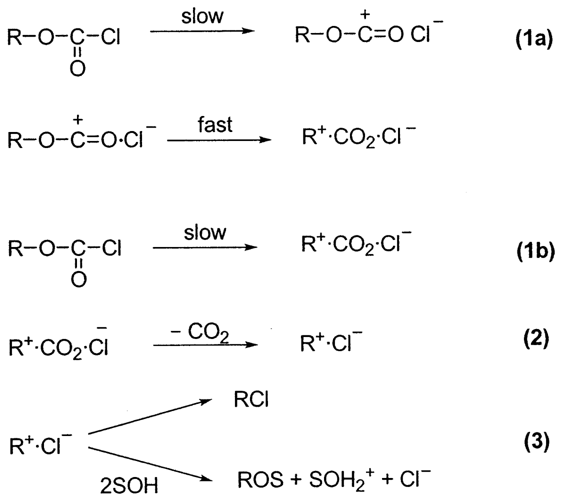
SCHEME 2



contribution to be made toward the question as to whether chloroformate esters, when reacting with loss of carbon dioxide, have a rate-determining concerted process, proceeding directly to $R^+CO_2Cl^-$, or whether there is a stepwise process, involving an initial rate-determining ionization to $(ROCO)^+Cl^-$, followed by a rapid loss of carbon dioxide. The study of 2-adamantyl chloroformate is simplified relative to that of isopropyl chloroformate in that elimination reaction to alkene is avoided, as a result of the prohibitively high ring strain that would be introduced by a double bond at the bridgehead (Bredt's rule). The slower reactions, relative to 1-adamantyl chloroformate as the substrate, allow an extension of the kinetic studies to binary solvents with fairly high water content (limited by solubility considerations) and to TFE−water solvents.

Results

The specific rates of solvolysis of 2-adamantyl chloroformate, at 25.0 °C, were determined in methanol and ethanol and in binary aqueous solvents with the other component being methanol, ethanol, acetone, or TFE. Determinations were also made in TFE−ethanol mixtures. The specific rates in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were too high for measurement by conventional sampling and titration of developed acid. In Table 1 are presented the 23 data points used in the linear free energy correlations and, when corresponding data are available for the 1-adamantyl chloroformate solvolysis−decomposition,[7] the specific rate ratio for the 1-adamantyl ester relative to that for the 2-adamantyl ester ($k_{1\text{-Ad}}/k_{2\text{-Ad}}$). For the reactions in MeOH, EtOH, and 80% EtOH, specific rates were also determined at 35.0, 45.0, and 55.0 °C, and these values, together with calculated enthalpies and entropies of activation, are reported in Table 2.

The products from the reactions of 2-adamantyl chloroformate under solvolytic conditions, at 25.0 °C, in ethanol and TFE and in a range of compositions for binary aqueous mixtures with ethanol, acetone, and TFE are reported in Table 3. Also contained are the results from a study across the full range of compositions for TFE−ethanol mixtures. After more than 10 half-lives for loss of substrate, the product analyses were carried out, with use of response-calibrated GLPC.

TABLE 1. Specific Rates of Solvolysis−Decomposition of 2-Adamantyl Chloroformate at 25.0 °C, N_T and Y_{Cl} Values, and the Specific Rate Ratio Relative to 1-Adamantyl Chloroformate ($k_{1\text{-Ad}}/k_{2\text{-Ad}}$)

solvent[a]	$10^5\,k$, s^{-1} [b]	N_T[c]	Y_{Cl}[d]	$k_{1\text{-Ad}}/k_{2\text{-Ad}}$
100% MeOH	5.38 ± 0.18[e]	0.17	−1.17	63
90% MeOH	9.16 ± 0.08	−0.01	−0.18	139
80% MeOH	17.0 ± 1.0	−0.06	0.67	
70% MeOH	28.0 ± 0.8	−0.40	1.46	
60% MeOH	56.1 ± 0.9	−0.54	2.07	
100% EtOH[f]	1.18 ± 0.02	0.37	−2.52	46
90% EtOH	2.97 ± 0.08	0.16	−0.94	99
80% EtOH	4.28 ± 0.21	0.00	0.00	280
70% EtOH	6.18 ± 0.20	−0.20	0.78	
60% EtOH	9.93 ± 0.59	−0.38	1.38	
50% EtOH	20.9 ± 0.4	−0.58	2.02	
90% acetone	0.358 ± 0.021	−0.35	−2.39	1168
80% acetone	1.00 ± 0.08	−0.37	−0.80	1460
70% acetone	2.70 ± 0.08	−0.42	0.17	
60% acetone	6.98 ± 0.30	−0.52	1.00	
97% TFE[g]	84.8 ± 9.7	−3.30	2.83	
90% TFE[g]	79.8 ± 1.3	−2.55	2.85	
70% TFE[g]	84.1 ± 6.0	−1.98	2.96	
50% TFE[g]	122 ± 19	−1.73	3.16	
80T−20E[h]	17.3 ± 0.6	−1.76	1.89	
60T−40E[h]	3.38 ± 0.24	−0.94	0.63	
40T−60E[h]	1.46 ± 0.10	−0.34	−0.48	475
20T−80E[h]	0.946 ± 0.039	0.08	−1.42	219

[a] With a substrate concentration of ca. 0.005 M and, unless otherwise stated, for mixed aqueous solvents, X% of organic solvent mixed with (100 − X)% of H_2O on a volume−volume basis at 25.0 °C. [b] With associated standard deviation. [c] From refs 11 and 12. [d] From refs 13 and 14. [e] In 100% MeOD, value of 2.87 ± 0.03 for a k_{MeOH}/k_{MeOD} ratio of 1.87 ± 0.08. [f] Values of 1.38 ± 0.01, 1.44 ± 0.03, 1.51 ± 0.01, and 2.23 ± 0.01 in the presence of 0.01, 0.02, 0.04, and 0.08 mol dm^{-3} Et_4NCl, respectively. [g] On a weight−weight basis. [h] 2,2,2-Trifluoroethanol (T)−ethanol (E) mixtures, by volume at 25.0 °C.

TABLE 2. Specific Rates of Solvolysis−Decomposition of 2-Adamantyl Chloroformate at Various Temperatures and Enthalpies ($\Delta H^\ddagger$, kcal/mol) and Entropies ($\Delta S^\ddagger$, eu) of Activation

solvent[a]	T, °C	$10^5\,k$, s^{-1} [b]	$\Delta H^\ddagger_{298}$[c]	$\Delta S^\ddagger_{298}$[c]
100% MeOH	25.0	5.38 ± 0.18[d]		
	35.0	14.5 ± 0.2		
	45.0	31.9 ± 1.2		
	55.0	90.6 ± 2.4	17.4 ± 0.1	−19.7 ± 0.4
100% EtOH	25.0	1.18 ± 0.02[d]		
	35.0	3.45 ± 0.12		
	45.0	9.03 ± 0.09		
	55.0	23.5 ± 0.3	18.7 ± 0.1	−18.4 ± 0.2
80% EtOH	25.0	4.28 ± 0.21[d]		
	35.0	14.2 ± 0.6		
	45.0	42.6 ± 2.4		
	55.0	110 ± 8	20.5 ± 0.1	−9.8 ± 0.3

[a,b] See footnotes to Table 1. [c] With associated standard error. [d] From Table 1.

For the aqueous alcohol solvents, selectivity values (S) were calculated according to eq 1, and for the reaction

$$S = \frac{[\text{adamantyl alkyl ether}][H_2O]}{[\text{adamantanol}][\text{alcohol}]} \qquad (1)$$

in TFE−ethanol, eq 2 was used. In both equations, the

$$S = \frac{[AdOCH_2CF_3][EtOH]}{[AdOEt][TFE]} \qquad (2)$$

TABLE 3. Percentages of Products in Solvolysis−Decomposition of 0.0025 M 2-Adamantyl Chloroformate at 25.0 °C

solvent[a]	2-AdOTFE (3.4)[b]	2-AdOEt (4.6)[b]	2-AdCl (6.2)[b]	2-AdOH (6.6)[b]	2-AdOCO-OEt (38.0)[b]
100% EtOH		5.9	4.8	1.3	88.0
90% EtOH		7.5	6.9	23.7	61.9
80% EtOH		10.7	13.5	37.8	38.0
70% EtOH		11.4	17.0	49.6	22.1
60% EtOH		11.5	16.7	59.3	12.5
50% EtOH		9.2	18.7	66.5	5.7
80% acetone			31.0	69.0	
60% acetone			31.2	68.8	
100% TFE	41.1		58.9		
97% TFE[c]	37.7		51.9	10.5	
90% TFE[c]	34.6		45.2	20.2	
70% TFE[c]	19.5		28.3	52.2	
50% TFE[c]	12.1		19.8	68.1	
80T−20E[d]	38.3	7.4	54.3		
60T−40E[d]	27.6	14.5	56.5		1.3
40T−60E[d]	15.4	22.6	46.8		15.2
20T−80E[d]	3.7	17.2	19.1	2.9	57.2

[a] Unless otherwise indicated, for mixed aqueous solvents, X% of organic solvent mixed with (100 − X)% of H_2O on a volume−volume basis at 25.0 °C; the reported values are the averages from duplicate analyses. [b] Retention time (min) under the GLPC conditions. [c] On a weight−weight basis. [d] 2,2,2-Trifluoroethanol (T)−ethanol (E) mixtures, by volume, at 25.0 °C.

TABLE 4. Selectivity Values for Ionization Pathway (S_{ion}) for Solvolyses in Solvents Containing 2,2,2-Trifluoroethanol and Comparison with Corresponding Values for Solvolyses of 1-Adamantyl Chloroformate ($S_{1\text{-}Ad}$) and Benzyl Chloroformate (S_{Bz})

solvent[a]	S_{ion}[b]	$S_{1\text{-}Ad}$[c]	S_{Bz}[d]
97% TFE	0.62		1.05
90% TFE	1.06		1.01
80% TFE		1.03	1.02
70% TFE	0.89		1.04
50% TFE	0.99		1.20
90T−10E			0.81
80T−20E	1.62		0.83
70T−30E		1.64	
60T−40E	1.58		0.73
50T−50E		1.46	
40T−60E	1.28		
30T−70E			1.29
20T−80E	1.07	1.13	

[a] Weight percentages for TFE−H_2O compositions and volume percentages for TFE−ethanol (T−E) compositions. [b] From eqs 2 and 3. [c] From ref 7b. [d] From ref 5.

product concentrations are divided by the concentration of the solvent component producing them, with all of the concentrations expressed as molarities.

Discussion

Product Studies in Solvents Containing 2,2,2-Trifluoroethanol (TFE). The percentages of the observed products are reported in Table 3. In 100% TFE only 2-adamantyl 2,2,2-trifluoroethyl ether and 2-adamantyl chloride were observed, and for solvolyses in the four aqueous−TFE solvents, these products were accompanied by 2-adamantanol. There was no evidence for formation of 2-adamantyl 2,2,2-trifluoroethyl carbonate. In 80% TFE−20% ethanol, only the two possible ether products plus 2-adamantyl chloride were observed. With higher ethanol content, increasing amounts of 2-adamantyl ethyl carbonate, formed by bimolecular attack at the acyl carbon, were observed, and indeed, this became the dominant product in 20% TFE−80% ethanol.

In the TFE−H_2O mixtures, the percentages of 2-adamantyl chloride, formed by loss of CO_2 and collapse, fall from 58.9% in 100% TFE to 19.8% in 50% TFE (by weight). The lack of any sensitivity toward changes in solvent nucleophilicity in the correlation analysis of specific reaction rates in these mixtures, using eq 3

$$\log(k/k_0) = lN_T + mY_{Cl} + c \qquad (3)$$

(discussed later),[10] indicates an ionization route and the falloff is possibly due to the smaller water molecules being more efficient in solvating the chloride anion, leading to separation being increasingly favored relative to collapse as the water content is increased. In eq 3, k and k_0 are the specific rates of solvolysis plus decomposition in a given solvent and in 80% ethanol, respectively; l is the sensitivity to changes in solvent nucleophilicity (N_T);[11,12] m is the sensitivity to changes in solvent ionizing power (Y_{Cl});[13,14] and c is a constant (residual) term. The selectivities (S) for TFE attack relative to water (eq 1) are almost constant (Table 4), with a value of 0.62 in 97% TFE (water slightly favored) rising to an essentially constant value of 0.98 ± 0.09 for the 90%−50% TFE range. The lack of any appreciable sensitivity, despite the much greater nucleophilicity of water, suggests that the solvolysis products are determined by a mechanism within which a molecule that has inserted into the intimate ion pair, to convert to the solvent-separated ion pair,[15] is then the one which rapidly captures the cation to give the final product.

For the TFE−ethanol mixtures, one can directly assess the extent of bimolecular attack at the acyl carbon because this leads to the stable 2-adamantyl ethyl carbonate. The alternative mixed carbonate, 2-adamantyl 2,2,2-trifluoroethyl carbonate, was not observed. This is consistent with earlier studies of attack at the acyl carbon of chloroformate esters in TFE−ethanol mixtures. For example, for the solvolyses of *p*-nitrobenzyl chloroformate[5] at 25.0 °C in 80% TFE−20% ethanol, only 1.1% of *p*-nitrobenzyl 2,2,2-trifluoroethyl carbonate was observed, falling to only trace amounts in 60% TFE−40% ethanol. The products other than the mixed carbonate arise from the ionization pathway, and one can calculate that, within this pathway, the percentages of collapse to 2-adamantyl chloride show only a slight falloff as one goes from 100% TFE in 20% intervals to 100% ethanol, with percentages of 58.9, 54.3, 57.2, 55.2, 47.7, and 44.9 (the 100% ethanol value is from Table 5). This is a remarkably small decrease considering the large in-

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TABLE 5. For Ionization Pathway (I), Estimates of 2-Adamantanol and 2-Adamantyl Chloride Formation, Estimated Percentage of Reaction by the Bimolecular Pathway, and Selectivity Value for This Pathway[a]

solvent	% 2-AdOH (I)	% 2-AdCl (I)	2-AdCl/ 1-AdCl[b]	bimol	S_{Bimol}
100% EtOH		44.9	1.10	89.2	
90% EtOH	4.3	36.9	1.05	83.9	1.15
80% EtOH	12.1	37.2	1.14	63.7	1.20
70% EtOH	20.2	35.1	1.18	51.5	1.04
60% EtOH	29.0	29.2	1.09	42.8	0.89
50% EtOH	33.7	30.4	1.29	38.5	0.56

[a] Using eq 4. [b] Comparison of the percentages of 2- or 1-adamantyl chloride formation from the ionization reactions of the chloroformate esters.

creases in solvent nucleophilicity and large decreases in solvent ionizing power over this range of solvent composition.

From a consideration of the percentages of the two solvolysis products, one can calculate (using eq 2), for each solvent composition, the selectivity values (TFE capture relative to ethanol capture). These values (Table 4) are very much larger than the vanishingly small values for bimolecular attack at the acyl carbon, and as with the TFE–water values, they are not far removed from unity, with a slight preference for TFE attack being indicated by values ranging from 1.62 (80% TFE–20% ethanol) to 1.07 (20% TFE–80% ethanol).

For both TFE–water and TFE–ethanol mixtures, the *S* values are very similar to the values observed from reactions of both 1-adamantyl[7] and benzyl[5] chloroformates under the same conditions (Table 4). Similarly, the data for several TFE–water mixtures for the collapse leading to 2-adamantyl chloride formation allow an interpolated value of 34.0% for 80% TFE (Table 3) to be estimated, a value only 40% higher than the value for 1-adamantyl chloroformate reaction.[7] The range of 52%–20% formation of 2-adamantyl chloride (Table 3) is only slightly higher than the range of 46%–15% formation of benzyl chloride from benzyl chloroformate for the identical range of solvent composition from 97%–50% TFE (by weight).[5] The range of 58.9%–44.9% for TFE–ethanol mixtures can be compared to an essentially constant value of 42% (±3%) for reactions of 1-adamantyl chloroformate, higher by only 40%–10% for the 2-adamantyl substrate. Similarly, for solvents in the range of 90% TFE–10% ethanol to 60% TFE–40% ethanol, benzyl chloroformate reaction leads to 46% (±3%) benzyl chloride formation.

It can be concluded on the basis of both *S* values for the solvolysis products and the percentages of reaction involving collapse to the alkyl chloride that the ionization pathways are remarkably similar in character for the tertiary bridgehead-substituted 1-adamantyl chloroformate,[7] the secondary bridge-substituted 2-adamantyl chloroformate, and the primary arylalkyl benzyl chloroformate.[5]

Product Studies in Ethanol–Water Mixtures. In accord with the earlier 1-adamantyl chloroformate study,[7] solubility considerations limited the range of the present study to a range from 100%–50% ethanol. Unlike the earlier study, the products obtained over the full range of compositions showed that appreciable amounts of attack at the acyl carbon accompanied the ionization pathway. For the 1-adamantyl chloroformate, only in 100% ethanol was a small amount (0.7%) of the mixed carbonate ester formed. The amounts of the 2-adamantyl ethyl carbonate in the present study range from 88% in 100% ethanol to 5.7% in 50% ethanol. In 100% ethanol, a small amount of 2-adamantanol (1.3%) was found, and since no 2-adamantanol was found for reaction in 100% TFE, this would appear to be due to the presence of a small concentration of water in the ethanol. It is well-documented that it is extremely difficult to get and to maintain ethanol with a very low water content.[16]

In aqueous ethanol, the amounts of mixed carbonate ester allow only a minimum measure of the extent of bimolecular attack at the acyl carbon since attack by water leads to the alkyl hydrogen carbonate, which very rapidly loses CO_2 to give the alcohol.[17] Accordingly, the 2-adamantanol will be formed by two independent pathways: ionization with CO_2 loss, followed by capture of the carbocation by water, and the formation of the hydrogen carbonate by attack at the acyl carbon, followed by the loss of CO_2.

The observation (Table 4) that the *S* values for solvent capture in the ionization route are essentially identical for the 1-adamantyl and 2-adamantyl chloroformates as the initial substrate, for both TFE–water and TFE–ethanol systems, is taken as an indication that this will also be the case for the reactions in ethanol–water mixtures. Since the 1-adamantyl chloroformate solvolyses have previously been shown to proceed with ionization, loss of CO_2, and capture of the formed carbocation, we can apply the *S* values obtained in that study, together with the percentages of 2-adamantyl ethyl ether obtained in the present study (Table 3) to estimate the amount of the total experimental determination of 2-adamantanol that results from ionization. The remaining 2-adamantanol ($2\mathrm{AdOH}_{\mathrm{bimol}}$) found to be present can then be assigned to the reaction pathway passing through the 2-adamantyl hydrogen carbonate. In turn, these values can be combined with the measured amounts of 2-adamantyl ethyl carbonate to arrive at a series of S_{bimol} values for attack at the acyl carbon, calculated from eq 4. The values decrease slightly with increasing water

$$S_{\mathrm{bimol}} = \frac{[\text{2-AdOCO}_2\text{Et}][\mathrm{H_2O}]}{[\text{2-AdOH}_{\mathrm{bimol}}][\mathrm{EtOH}]} \tag{4}$$

content, with a value of 1.15 for 90% ethanol, decreasing to 0.56 for 50% ethanol (Table 5).

Previous *S* values for attack at the acyl carbon of chloroformate esters have been rather larger, with values of 2.0 to 4.1 for benzyl chloroformate in 90%–50% ethanol,[5] 4.1 and 6.1 for *p*-nitrobenzyl chloroformate in 80% and 60% ethanol,[5] and 2.6 and 4.2 for *p*-nitrophenyl chloroformate in 80% and 60% ethanol.[18] The lower *S* value for attack at the acyl carbon in the present study 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

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solvolysis of 1-adamantyl chloroformate in these solvents proceeds entirely by the ionization pathway and values for this substrate are not available for comparison.

Product Studies in Aqueous Acetone. Only two products, 2-adamantyl chloride and 2-adamantanol, are observed. The percentages are essentially identical in 80% and 60% acetone. The relatively large 31% of 2-adamantyl chloride suggests a dominant ionization mechanism.

The 2-AdCl/1-AdCl product formation ratio of 1.14 (±0.09) in aqueous ethanol mixtures can be combined with the 31.7% of 1-adamantyl chloride formation from reaction of 1-adamantyl chloroformate in 80% acetone[7] to arrive at an estimated value of 36% for 2-adamantyl chloride formation from 2-adamantyl chloroformate in the ionization pathway, suggesting that about 86% of the overall reaction of 2-adamantyl chloroformate in 80% acetone is by the ionization route.

Kinetic Studies. The specific rates of solvolysis−decomposition are similar to those obtained in a parallel study[6] with isopropyl chloroformate as the substrate. For the solvents in Table 1 that do not contain TFE, isopropyl chloroformate reacts faster by a factor of 2.1−5.2. A lower value of 0.84 is observed for 97% TFE, and this gradually rises to a value of 1.4 for 70% TFE (no isopropyl value available for 50% TFE). A similar trend is observed for TFE−ethanol mixtures, with a value of 1.2 in 80T−20E rising to a value of 3.3 in 20T−80E.

These very small ratios can be compared with values for the same range of solvents for solvolyses of the corresponding *p*-toluenesulfonates. Values are found to vary in the same manner but over a considerably expanded range of values: the isopropyl ester solvolyzes faster by a factor of 910 in ethanol and the 2-adamantyl ester by a factor of 2.5 in 97% TFE.[19−21] The explanation in terms of nucleophilic assistance being important in the solvolyses of the isopropyl ester but not in the solvolyses of the 2-adamantyl ester was supported by m values (sensitivity to solvent ionizing power changes) of 1.00 (standard) for 2-adamantyl *p*-toluenesulfonate and 0.48−0.28, depending on the solvents included in the correlation, for the isopropyl ester.[20] In the present study, the reduced ratio in ethanol is consistent with the principal pathway involving nucleophilic attack at the acyl carbon and, for the solvolyses with ionization in 97% TFE, the reduced value results from a lower demand for assistance from solvolysis of the incipient cation due to the driving force and earlier transition state resulting from the accompanying fragmentation.

TABLE 6. Correlations Using One-Term and Two-Term Grunwald−Winstein Equations for Solvolysis−Decomposition of 2-Adamantyl Chloroformate and Comparison with Ionization Pathways for Related Solvolyses

substrate	n[a]	l[b]	m[b]	c[b,c]	R[d]
2-AdOCOCl	23[e]		0.40 ± 0.03	0.04 ± 0.27	0.9288
2-AdOCOCl	23[e]	0.04 ± 0.10[f]	0.41 ± 0.05	0.06 ± 0.28	0.9293
2-AdOCOCl	19[g]		0.47 ± 0.03	−0.11 ± 0.19	0.9703
2-AdOCOCl	19[g]	0.03 ± 0.07[f]	0.48 ± 0.04	−0.10 ± 0.19	0.9706
2-AdOCOCl	7[h]		0.55 ± 0.03	−0.32 ± 0.10	0.9934
2-AdOCOCl	17[i]		0.52 ± 0.02	0.10 ± 0.14	0.9885
1-AdOCOCl[j]	15[k]		0.47 ± 0.03	0.03 ± 0.05	0.985
i-PrOCOCl[j]	20[l]	0.28 ± 0.05	0.52 ± 0.03	−0.12 ± 0.05	0.979
BzOCOCl[j]	11[m]	0.25 ± 0.05	0.66 ± 0.06	−2.05 ± 0.11	0.976
EtOCOCl	7[n]	0.69 ± 0.13	0.82 ± 0.16	−2.40 ± 0.27	0.946
EtSCOCl	19[n]	0.66 ± 0.08	0.93 ± 0.07	−0.16 ± 0.31	0.961
PhSCOCl	6[o]	0.62 ± 0.08	0.92 ± 0.11	−2.29 ± 0.13	0.983
PhOCSCl	8[p]	0.43 ± 0.06	1.19 ± 0.08	−3.14 ± 0.12	0.991
PhSCSCl	14[p]	0.55 ± 0.09	0.84 ± 0.08	0.07 ± 0.24	0.967

[a] Number of data points used in the correlation. [b] From eq 3. [c] Accompanied by the standard error of the estimate; the appreciably negative values are due to the partial or dominant operation of the bimolecular mechanism in the standard solvent (80% ethanol). [d] Correlation coefficient. [e] All solvents of Table 1. [f] Probability that the lN term is not statistically significant of 0.70. [g] Omitting the 100% and 90% EtOH and 100% and 90% MeOH data points. [h] In the solvents containing TFE (excluding 20T−80E). [i] In ethanol−water (adjusted values), acetone−water, and solvents containing TFE (20T−80E value adjusted), see text. [j] solvolysis−decomposition. [k] From refs 6 and 7. [l] From ref 6. [m] From ref 5. [n] From ref 2. [o] From ref 24. [p] From ref 25.

Another ratio that is potentially useful involves a comparison of the specific rates of solvolysis of the 1-adamantyl and 2-adamantyl derivatives ($k_{1\text{-Ad}}/k_{2\text{-Ad}}$). For *p*-toluenesulfonates or methanesulfonates, a value of close to 10^5 has been found to apply for a variety of solvents.[22,23] In the present study, the values for the chloroformates are in the range of 46−1460 (Table 1). The lower values in this range are misleading because of a large bimolecular contribution being involved for the 2-adamantyl chloroformate solvolyses. When the estimated values for the ionization pathway are obtained by multiplying the overall specific rates (Table 1) by the fraction of ionization reaction (1-Bimol/100), with the percentage of bimolecular reaction (Bimol) from Table 5, the aqueous ethanol values become 427 (100% EtOH), 530 (90% EtOH), and 773 (80% EtOH). For the 40T−60E and 20T−80E compositions, the Bimol values are the percentages of 2-adamantyl ethyl carbonate from Table 3 and ionization pathway values of 559 and 512 are obtained. The estimate of 86% of reaction occurring by the ionization route with 2-adamantyl chloroformate in 80% aqueous acetone suggests that the 90% acetone and 80% acetone ratios of 1168 and 1460 (Table 1) will be only slightly lower than the values for the ionization pathway.

To a rough approximation, we can say that the $k_{1\text{-Ad}}/k_{2\text{-Ad}}$ ratio of about 10^5 for tosylates and mesylates is reduced to values in the 4×10^2 to 1.5×10^3 region for the solvolysis−decomposition constituting the ionization pathway for the chloroformate esters.

The specific rates of solvolysis−decomposition (Table 1) have been analyzed in terms of the two-term and one-term Grunwald−Winstein equation (eq 3, with and without the lN_T term). The sensitivities obtained in these correlations are reported, together with values previously obtained for other chloroformate esters,[2,5−7] and some sulfur-for-oxygen substituted derivatives,[2,24,25] in Table 6. With all 23 solvent systems included, moderately good correlations are obtained, with an m value of 0.40 ± 0.03

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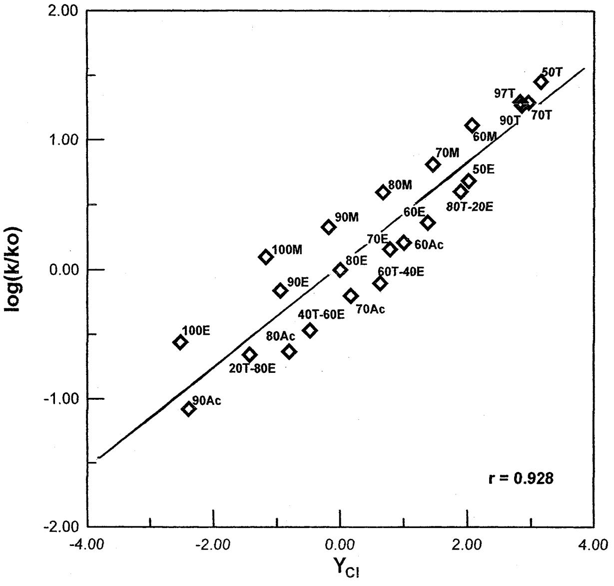

FIGURE 1. Plot of log(k/k_0) for solvolysis of 2-adamantyl chloroformate in all solvents against Y_{Cl} values.

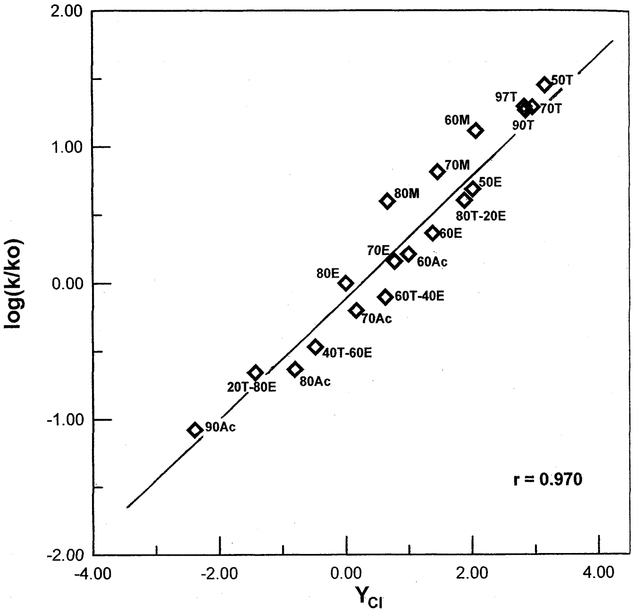

FIGURE 2. Plot of log(k/k_0) for solvolysis of 2-adamantyl chloroformate against Y_{Cl} values, with omission of the four data points for 100% and 90% ethanol and methanol.

for the one-term equation (Figure 1). For the two-term equation, values are obtained of 0.41 ± 0.05 for m and 0.04 ± 0.10 for l, corresponding to a 0.70 probability that the lN_T term is statistically insignificant.

Inspection of the data shows that the four data points previously[6] excluded from the correlations of the specific rates of isopropyl chloroformate solvolysis–decomposition, 100% and 90% ethanol and 100% and 90% methanol, also lie above the correlation plot shown in Figure 1. Exclusion of these points leads to a one-term m value of 0.47 ± 0.03 (correlation coefficient of 0.9703; Figure 2). Application of the two-term equation leads to negligible improvement in the correlation, again with a 0.70 probability that the lN_T term is statistically insignificant and with a fall in the F-test value from 274 to 130.

Despite the good correlations for these 19 solvents, the product studies have indicated appreciable bimolecular contributions to some of the included solvolyses. The bimolecular contribution is as much as 64% for 80% ethanol (Table 5) and 57% for 20% TFE–80% ethanol (Table 3). To avoid any appreciable bimolecular contribution, we have repeated the correlation analysis using only the seven data points for solvents containing TFE other than 20T–80E. An excellent one-term correlation is obtained (Table 6) with an m value of 0.55 ± 0.03 and a correlation coefficient of 0.9934 (F-test value of 226). The number of solvents available for this correlation of strictly ionization values can be increased by extracting the ionization component from the aqueous ethanol and 20T–80E specific rates (Table 1). This can be done by multiplying the experimental values by the fraction of ionization reaction (Tables 3 and 5). Also including the two aqueous acetone data points from Table 1, we obtain, for 17 solvents, an m value of 0.52 ± 0.02 for the one-term correlation and a correlation coefficient of 0.9885 (F-test value of 378).

The range of operation for the bimolecular mechanism is not wide enough to allow a meaningful application of the two-term Grunwald–Winstein equation. Previous values for other chloroformate esters for which this pathway is believed to be favored over a wide range of solvent types have given, for analyses of the data in those solvents favoring bimolecular attack, almost identical l values of 1.68, 1.59, and 1.56, and m values of 0.57, 0.58, and 0.55 for the solvolyses of phenyl,[4] methyl,[1] and ethyl[2] chloroformates, respectively. The m values are essentially identical to those obtained in the present study for the ionization pathway, and coupled with the knowledge that the N_T values applicable to the bimolecular pathway vary by less than 1 order of magnitude as one goes from 100% ethanol to 50% ethanol (Table 1), it can be understood why the change from the initially dominant bimolecular mechanism to the ionization mechanism occurs only very gradually as one increases the water content of the aqueous ethanol solvents (values in Table 5 show a gradual decrease from 89% bimolecular for 100% ethanol to 39% bimolecular for 50% ethanol).

Mechanism of the Ionization Route for Solvolysis–Decomposition. Compelling evidence has been outlined earlier, based on leaving-group effects, that the ionization pathway does not involve ionization to an adamantyl cation plus the chloroformate anion, followed by loss of CO_2 from the anion. The considerably faster reaction of the chloroformate[7] relative to either the fluoroformate[8] or the trifluoroacetate[26] is incompatible with the estimated relative leaving-group efficiencies of the anions that would be involved. In the ionization pathway, 1-adamantyl chloroformate reacts 10^4–10^5 times faster than the fluoroformate,[8] suggesting an important contribution from carbonyl carbon–halogen bond-breaking in the rate-determining step.

The choice between the two remaining pathways (Scheme 2) involves initiation of reaction either by a stepwise loss of chloride ion, followed by loss of CO_2 from the carboxylium cation (step 1a of Scheme 2) or by a concerted loss of chloride ion and carbon dioxide (step

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1b of Scheme 2). In both instances the $R^{+}\cdot CO_2\cdot Cl^{-}$ then proceeds to the observed products by steps 2 and 3 of Scheme 2.

Although there is no single piece of compelling evidence in favor of a concerted process, we believe that the overall evidence, largely involving comparisons with other systems, is strongly in favor of this pathway. Both the 1-adamantyl and 2-adamantyl chloroformate pathways for solvolysis−decomposition give one-term Grunwald−Winstein plots with *m* values of about 0.5. In other solvolysis studies, low *m* values have been rationalized in terms of an early transition state involving, for unimolecular solvolyses, intramolecular assistance to the ionization process. For example, in the solvolyses of *N*,*N*-diphenylcarbamoyl chloride (Ph_2NCOCl), nucleophilic interaction of the lone pair of electrons on the nitrogen led[27] to an ionization pathway with an *l* value of 0.23 ± 0.04 and an *m* value of 0.58 ± 0.03 (correlation coefficient of 0.971). Even lower *m* values (0.33−0.47) have been observed[28] when there is sulfur participation (k_Δ process[29]) in the solvolyses of mustard chlorohydrins.[30]

An *m* value of 0.52 ± 0.03 was observed[6] in the solvolyses of isopropyl chloroformate, accompanied by an *l* value of 0.28 ± 0.05, a typical *l* value for a moderate nucleophilic solvation of a developing carbocation and a value considerably lower than the value of 0.53 for the correlation of the specific rates of solvolysis of isopropyl *p*-toluenesulfonate.[20] In contrast, solvolyses of both 1-adamantyl and 2-adamantyl chloroformates have negligible *l* values. This could be explained by additional steric hindrance to solvation at the acyl carbon, relative to the isopropyl substrate, but it is best explained in terms of the rate-determining step being according to step 1b of Scheme 2, such that there is appreciable nucleophilic solvation of the developing isopropyl cation but the usual[20,21] negligible solvation of the incipient adamantyl cations. Since the specific rates of solvolysis of AdX compounds are used to establish Y_X scales,[13] it follows that the *l* values of the two-term Grunwald−Winstein equation are set at zero for these solvolyses, and the essentially zero value of the present study (Table 6) is nicely consistent with a concerted ionization−loss of CO_2 process.

The 1-Ad/2-Ad ratio of about 10^3, as opposed to 10^5 for the solvolyses of sulfonate esters, is also consistent with the concerted process, in which the ejection of CO_2 in the rate-determining step leads to an earlier transition state and not only lower *m* values but also the observation of an appreciable 1-Ad/2-Ad ratio, but considerably less than the maximum, which would be observed for the late transition state of a conventional ionization.[31]

It is instructive to compare the correlations of the specific rates of solvolysis of the two adamantyl chloroformates and isopropyl chloroformate with the correlations of the specific rates of solvolysis of chloroformate esters, which are believed to exhibit ionization behavior but without concurrent loss of CO_2. For example, ethyl chloroformate and ethyl chlorothioformate[2] are very unlikely to fragment to an ethyl cation, and fragmentation to a phenyl cation in the ionization reactions of sulfur-for-oxygen substituted phenyl chloroformate[24,25] is highly unlikely. These compounds, when reacting with ionization, all give very similar two-term correlations (eq 3), with appreciable nucleophilic solvation (*l* values of 0.43−0.69), presumably reflecting nucleophilic solvation at the acyl carbon, and a high dependence on solvent ionizing power (*m* values of 0.82−1.19), essentially the same as in conventional ionization reactions at an sp^3-hybridized carbon.[12] The nature of the very different correlations for the ionization reactions of the secondary and tertiary alkyl chloroformates from those for primary and phenyl chloroformates strongly supports the concept that fragmentation accompanies the ionization of the former but not of the latter.

It is of interest to compare the solvolysis−decomposition reactions of alkyl chloroformates with those for alkoxychlorocarbenes, generated in situ by photolysis of 3-alkoxy-3-chlorodiazirines.[32] The carbenes are already of high energy content, and only low activation energies are involved in their fragmentations to $R^{+}Cl^{-}$ ion pairs, associated with a carbon monoxide molecule (eq 5). These

$$\mathrm{RO\ddot{C}Cl} \rightarrow \mathrm{R^{+}COCl^{-}} \qquad (5)$$

fragmentations will have early transition states, and the variation of the fragmentation rate for a series of R groups of very different stabilities as R^{+} has been shown to be surprisingly modest.[33]

For the reactions of a series of bridgehead R groups within the carbene, it was found that the situation paralleled that for 2-adamantyl chloroformate in that the solvolysis−decomposition can be accompanied by bimolecular attack at the carbon that would have been lost in the fragmentation. In methanol, concentrating on the solvolysis−decomposition pathway, the RCl/ROMe ratio at 25.0 °C was 1.5 (60% RCl) from 1-adamantyloxychlorocarbene[34] and 0.34 (25% RCl) from 1-adamantyl chloroformate.[7] The difference may reflect the formation of a higher-energy and more reactive carbocation from the carbene and/or a reduced steric hindrance to collapse of the ion pair when the ejected molecule is carbon monoxide rather than carbon dioxide.

Conclusions

In the previously studied solvolyses of 1-adamantyl chloroformate,[7] an ionization with accompanying loss of carbon dioxide led to an ion pair. The 1-adamantyl cation was then captured either by the counterion to give decomposition product or by the solvent to give solvolysis product. Only in ethanol was a small amount of product, the mixed carbonate ester, requiring attack at the acyl carbon observed. Replacement of chlorine by fluorine[8] considerably reduced the ionization rate, and with little change in the rate of the addition−elimination reaction

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at the acyl carbon, in reasonably nucleophilic solvents substantial amounts of the bimolecular attack at acyl carbon were observed.

We now show that the movement toward bimolecular attack at acyl carbon can also be induced by replacing the tertiary 1-adamantyl group by the secondary 2-adamantyl group. In ethanol, 89% of the reaction now involves the bimolecular attack. On addition of water to the ethanol, the percentage falls rather slowly, reaching a value of 39% in 50% ethanol (by volume). There was no evidence for any bimolecular attack in the highly ionizing and weakly nucleophilic TFE or aqueous TFE solvents. In all solvents, a substantial amount of 2-adamantyl chloride was present among the products, ranging from 5% in 100% ethanol (constituting 45% of the ionization pathway products) to 59% in 100% TFE.

For the formation of solvolysis products by the ionization pathways that are totally dominant in TFE−water mixtures and dominant in all TFE−ethanol mixtures except 20% TFE−80% ethanol (by volume), the selectivity values are all close to unity. The values are very similar to those previously observed for the parallel ionization pathway reactions of benzyl chloroformate.[5] In aqueous ethanol, the values observed for the bimolecular pathway are also close to unity, reflecting a rather small difference between the nucleophilicities of the water and ethanol components of the solvent.

Analyses using the extended Grunwald−Winstein equation (eq 3) showed that the l value was negligible. With 100% and 90% ethanol and methanol omitted, an l value of 0.03 ± 0.07 was coupled with an m value of 0.48 ± 0.04. The two-term equation had essentially the same correlation coefficient (0.9706) as the one-term treatment against only solvent ionizing power values (0.9703). The l and m values parallel those for 1-adamantyl chloroformate and the m value is also similar to that observed for isopropyl chloroformate solvolyses.[6] However, for the isopropyl chloroformate solvolyses, an appreciable l value of 0.28 ± 0.05 was observed, suggesting a moderate solvation of a developing carbocation. The respective l values suggest that the solvation is of an incipient alkyl carbocation, consistent with a value of the magnitude observed for isopropyl chloroformate solvolysis and zero (by definition[13]) for a developing 1-adamantyl carbocation. The observed m values are much lower than for the ionization reactions observed for solvolyses of sulfur-for-oxygen derivatives of phenyl chloroformates,[24,25] where fragmentation to a phenyl cation is disfavored, leading to m values in the 0.8−1.2 region. This is consistent with a concerted fragmentation−ionization leading to an earlier transition state and reduced sensitivity to changes in solvent ionizing power.

When the ionization component of the reactions is considered, the 1-Ad/2-Ad rate ratio is in the region of 420−1460. This value is appreciable but considerably lower than the value of about 10^5 for solvolyses of sulfonate esters.[22,23,35] This reduction in value is also consistent with a concerted fragmentation−ionization leading to an earlier transition state, such that the incipient carbocation is less developed.

The favored interpretation of the presented study is in terms of step 1b rather than step 1a operating within Scheme 2. The overall scheme is then indirectly supported by the close parallel to the one proposed[33] for the methanolyses of bridgehead alkoxychlorocarbenes, where there is competition between a bimolecular attack at the carbene carbon and a concerted ionization−fragmentation pathway.

Experimental Section

Synthesis of 2-Adamantyl Chloroformate. A solution of 0.660 g of triphosgene in 20 mL of toluene at 0−4 °C (ice bath) was added to a room-temperature solution of 0.505 g of 2-adamantanol and 0.300 mL of pyridine in 20 mL of toluene, over a period of 1 h. The mixture was then extracted with 3 × 50 mL of ice water and dried (anhydrous $MgSO_4$). It was passed through a glass filter, and the toluene was removed using a rotary evaporator. The residue was recrystallized twice from anhydrous petroleum ether to give 0.427 g (60.0% yield) of white crystalline 2-adamantyl chloroformate, mp 44.6−45.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50−2.09 (m, 14), 3.87 (s, 1). IR (KBr) includes 2911, 2859, 1774 (C═O), 1160 (C−O), 964, 855, 691 cm^{-1}. Anal. Calcd for $C_{11}H_{15}O_2Cl$: C, 61.54; H, 7.04; O, 14.90. Found: C, 61.97; H, 6.93; O, 14.80.

The solvents were purified, and the kinetic runs carried out as previously described.[11]

Product Studies. The products from the reactions of 2-adamantyl chloroformate under solvolytic conditions were analyzed after 10 half-lives by gas chromatography using a 2.1-m glass column containing 10% Carbowax 20 M on Chromosorb WAW 80/100 with an injection temperature of 170 °C and column temperature of 120 °C. The retention times of observed products are reported in Table 3.

The 2-chloroadamantane and 2-adamantanol used in response calibration were recrystallized commercial materials. The other three products involved in the GLPC analyses were prepared by a general procedure involving solvolysis of 2-adamantyl chloroformate in ethanol or in TFE for 48 h at reflux. The solvent was then removed by evaporation under reduced pressure, and 20 mL of petroleum ether was added. The 2-adamantyl ethyl carbonate and 2-adamantyl ethyl ether[36] were separated and collected from the reaction in ethanol by GLPC, and the 2-adamantyl 2,2,2-trifluoroethyl ether[37] was similarly obtained from the reaction in TFE. The two light yellow liquid ether products were identified by NMR and IR, including comparison with literature spectral data.[36,37] The 2-adamantyl ethyl carbonate was a solid, mp 32.7−33.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54−2.09 (m, 14), 1.32 (t, 3, $J = 7.1$ Hz), 4.19 (q, 2, $J = 7.1$ Hz), 4.79 (s, 1). IR (KBr) includes 2910, 2860, 1735 (C═O), 1372, 1258 (C−O), 1098, 928, 793 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99; O, 21.40. Found: C, 69.21; H, 8.89; O, 21.90.

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