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Concerning the Two Reaction Channels for the Solvolyses of Ethyl Chloroformate and Ethyl Chlorothioformate

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The extended (two-term) Grunwald−Winstein equation has been applied to the solvolyses of ethyl chloroformate and ethyl chlorothioformate. For each substrate, there is evidence for two competing reaction channels. In ethyl chloroformate solvolysis, an addition−elimination channel dominates ($l = 1.56$, $m = 0.55$), and only in the more ionizing and least nucleophilic solvents does the principal reaction channel involve ionization, with an appreciable nucleophilic solvation of the developing acylium ion ($l = 0.69$, $m = 0.82$). For ethyl chlorothioformate, the relative importance of the two reaction channels is reversed, and, for the majority of solvents, the ionization pathway is dominant ($l = 0.66$, $m = 0.93$); only in methanol, ethanol, and 90% ethanol was the major pathway bimolecular. These observations are compared with those previously reported for the corresponding phenyl esters.

Because of convenient rates of reaction at temperatures close to ambient, chloroformate esters (ROCOCl) have been widely used in mechanistic studies of nucleophilic substitution reactions at acyl carbon, rather than the much more reactive acyl chlorides (RCOCl). The relatively slow reaction results primarily from a ground-state stabilization by resonance,[1,2] involving the lone-pair electrons on the oxygen adjacent to the carbonyl group. There have been several reports concerning the mechanism of solvolysis of ethyl chloroformate (eq 1). Reaction with an alcohol leads to a dialkyl carbonate and reaction

$$\mathrm{EtOCOCl} + 2\mathrm{SOH} \rightarrow \mathrm{EtOCOOS} + \mathrm{SOH_2}^{+} + \mathrm{Cl}^{-}$$

$$\mathrm{EtOCOOH} \rightarrow \mathrm{EtOH} + \mathrm{CO_2}\ (\text{when S} = \text{H})$$

with water to the ethyl hydrogen carbonate, which rapidly decomposes to CO_2 and ethanol.[3−5]

Leimu[6] showed the specific rate of methanolysis of ethyl chloroformate to be intermediate between those for the methyl and isopropyl esters (Me > Et > *i*-Pr), consistent with a bimolecular reaction in which bond-formation to the attacking nucleophile is the dominant aspect. Hall proposed[7] a bimolecular mechanism for hydrolysis, largely on the basis of a fairly large negative entropy of activation. Crunden and Hudson[5] found, in 35% aqueous acetone (65% water), a specific rate order of Me > Et < *i*-Pr and, in moist formic acid (1−2% water), a specific rate order of Me < Et ≪ *i*-Pr. They concluded that the isopropyl chloroformate reacted by a dominant S_N1 mechanism in both solvents, and ethyl chloroformate by a bimolecular mechanism in the aqueous acetone and by a unimolecular mechanism in the moist formic acid. Orlov[8] studied the ethanolysis of a series of halogenoformates, including ethyl chloroformate, and concluded that they all reacted by a bimolecular mechanism, involving rate-determining addition of the nucleophile within an addition−elimination sequence. Queen[9] reached an identical conclusion for the hydrolyses of a similar set of derivatives, plus he included isopropyl chloroformate which showed a positive entropy of activation (+10 eu) and a lower solvent isotope effect (k_{H_2O}/k_{D_2O}). This secondary alkyl ester was assumed, consistent with the earlier study,[5] to hydrolyze dominantly by the S_N1 mechanism. The entropy of activation value[9] of −17 eu observed for ethyl chloroformate was intermediate between previous values of −12 eu[7] and −24 eu.[10] Entropy of activation values are even more negative in methanol and ethanol (both −34 eu).[10]

Kivinen[10] noted that the kinetic behavior as either the solvent or the temperature was varied was similar to that for bimolecular solvolyses of alkyl halides, and he proposed a concerted S_N2 mechanism rather than the addition−elimination mechanism for the solvolyses of ethyl chloroformate and other acid chlorides. His value[11] for the solvent isotope effect (k_{H_2O}/k_{D_2O}) at 25.0 °C of 1.95 is in good agreement with the value of 1.82 subsequently reported by Queen;[9] large values for attack at acyl carbon have been suggested to be a consequence of two water molecules undergoing covalency changes, with one acting as a general base.[12] A parallel explanation has been given for large solvent k_{MeOH}/k_{MeOD} values.[13] Recently, Kivinen's proposal has been given support for the alcoholysis, aminolysis, and hydrolysis of acetyl chloride on the basis of both rate and product studies.[14] With good electron-supplying R groups within RCOCl, the bimo-

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lecular mechanism changes over to one which is essentially S_N1.[15]

This S_N1-S_N2 duality of mechanism involves mechanisms which both have extensive bond-breaking at the transition state, and relatively large halogen leaving-group effects should be observed. Consistent with this prediction, values for alcoholysis or hydrolysis of acetyl halides in binary solvents containing a relatively inert component are approaching 10^4 for k_{Cl}/k_F ratios and are in the region of 200−500 for k_{Br}/k_{Cl} ratios.[16]

For halogenoformates, very different k_{Cl}/k_F ratios have been observed. Hudson and Green[17] reported a value of 0.035 in 85% acetone at 0 °C for solvolyses of ethyl halogenoformates and, for ethanolysis, Orlov[8] reported values of 0.9 at 25.1 °C and 1.1 at 55.4 °C. These values have been uniformly interpreted in terms of a bimolecular addition−elimination mechanism, proceeding through a tetrahedral intermediate. The large differences in k_{Cl}/k_F ratios for solvolyses of carboxylic acid halides and halogenoformate esters, about 4 orders of magnitude, suggest fundamental differences in their solvolysis mechanisms and the need for a separate consideration of the solvolyses for each type of compound. In particular, Kivinen's claim[1,10] of S_N2 behavior appears to apply, at best, only for carboxylic acid halides[14] and not for the solvolyses in aqueous acetone or ethanol of ethyl halogenoformates.

A powerful tool in the consideration of the reaction mechanism for solvolysis reactions involves the use of the Grunwald−Winstein equation, especially in its extended form (eq 2). In eq 2, k and k_0 are the specific rates of

$$\log(k/k_0)_{RX} = lN_T + mY_X + c \qquad (2)$$

solvolysis of substrate RX in a given solvent and in the standard solvent (80% ethanol), respectively, l is the sensitivity toward changes in solvent nucleophilicity (N_T values being recommended[18,19]), m is the sensitivity toward changes in solvent ionizing power (Y_X scale[20] being applied for a leaving group X), and c is a constant (residual) term.

We have found[21] that eq 2 can be applied successfully ($R = 0.973$) to the specific rates of solvolysis of phenyl chloroformate over the full range of solvents commonly employed in this type of study. This is a solvolysis for which there is much evidence, including k_{Cl}/k_F ratios of about unity,[8] for an addition−elimination pathway.[9,22] The l and m values of 1.68 and 0.57, respectively, can be considered as representative values for an addition−elimination reaction of chloroformate esters. Extension[23] to corresponding solvolyses of the thiochloroformate ester (PhSCOCl) showed, despite the previous demonstration of S_N1 solvolyses in water,[24] the addition−elimination mechanism to be dominant in all but the least nucleophilic and/or most ionizing solvents. The ionization mechanism, with a strong nucleophilic solvation component, was found to be the dominant mechanism only in water and in fluoro alcohol-rich binary solvents ($l = 0.62$; $m = 0.92$).

We now report concerning the application of eq 2 to the solvolyses of ethyl chloroformate. In particular, we wish to see whether there is evidence from application of eq 2 for a change in mechanism in the more ionizing and/or weakly nucleophilic solvents, consistent with the claim for formolysis,[5] and whether the Grunwald−Winstein equation analyses of the bimolecular attack shows characteristics of addition−elimination[8,9,23] or S_N2[1,10] attack. Further, the study has been extended to ethyl chlorothioformate (EtSCOCl) to see whether the shift from bimolecular attack toward ionization, observed on introducing sulfur into phenyl chloroformate,[2,3,24] also manifests itself in the solvolyses of the ethyl esters.

Results

The specific rate of solvolysis of ethyl chloroformate was determined in 39 solvents at 24.2 °C. The solvents consisted of ethanol, methanol, formic acid, 2,2,2-trifluoroethanol (TFE), and binary mixtures with water of ethanol, methanol, TFE, acetone, dioxane, and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) plus four binary mixtures of TFE and ethanol. The specific rates of solvolysis are presented in Table 1, together with N_T[18,19] and Y_{Cl}[20,25] values.

The specific rates of solvolysis of ethyl chlorothioformate were measured at 25.0 °C in 21 solvents of the same general type as those used for ethyl chloroformate, except that formic acid and aqueous dioxane solvents were not included. The results are reported in Table 2, together with a specific rate in water, obtained by extrapolation using data reported earlier.[24] Also in Table 2 are presented the ratios of the specific rates for solvolyses of ethyl chlorothioformate at 25.0 °C and ethyl chloroformate at 24.2 °C (the latter from Table 1).

Discussion

The specific rate of solvolysis of ethyl chloroformate has previously been determined in several of the solvents of Table 1 at 24.5−25.0 °C. These values are presented as footnotes to Table 1, and they are all in good agreement with the values determined at 24.2 °C. An extrapolated (from higher temperatures[5]) specific rate of solvolysis in moist formic acid is also in reasonable agreement with our value for 100% formic acid.

For 35 of the solvents for which specific rates of solvolysis are reported, both N_T and Y_{Cl} values are available (listed in Table 1). A consideration in terms of the simple Grunwald−Winstein equation (eq 2 without the lN_T term) leads to an m value of 0.03 ± 0.08 (with a

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Table 1. Specific Rates of Solvolysis of Ethyl Chloroformate[a] in a Variety of Pure and Mixed Solvents at 24.2 °C and the N_T and Y_{Cl} Values for the Solvents

solvent[b]	$10^5\ k$, $s^{-1\ c}$	N_T[d]	Y_{Cl}[e]
100% EtOH	2.26 ± 0.05[f]	0.37	−2.52
90% EtOH	5.45 ± 0.09	0.16	−0.94
80% EtOH	7.31 ± 0.06	0.00	0.00
70% EtOH	9.95 ± 0.16	−0.20	0.78
60% EtOH	12.1 ± 0.2[g]	−0.38	1.38
40% EtOH	22.6 ± 0.7	−0.74	2.75
20% EtOH	33.1 ± 0.6[h]	−1.16	4.09
100% H_2O	34.2 ± 0.5[i]	−1.38	4.57
100% MeOH	8.24 ± 0.09[j]	0.17	−1.17
90% MeOH	16.7 ± 0.7	−0.01	−0.18
80% MeOH	24.6 ± 0.6	−0.06	0.67
60% MeOH	40.1 ± 1.3	−0.54	2.07
40% MeOH	54.0 ± 1.2	−0.87	3.25
20% MeOH	44.3 ± 2.5	−1.23	4.10
95% acetone	0.0747 ± 0.0019	−0.49	−3.19
90% acetone	0.298 ± 0.011	−0.35	−2.22
80% acetone	0.963 ± 0.010[k]	−0.37	−0.83
60% acetone	3.68 ± 0.10	−0.52	0.95
40% acetone	9.60 ± 0.12	−0.83	2.46
20% acetone	21.6 ± 0.5	−1.11	3.77
95% dioxane	0.198 ± 0.013		
90% dioxane	0.465 ± 0.014		
60% dioxane	5.41 ± 0.22	−0.54	
40% dioxane	13.5 ± 1.1	−0.84	
20% dioxane	24.2 ± 1.3	−1.12	3.71
100% HCOOH	0.199 ± 0.016[l]	−2.44	3.20
100% TFE	0.0180 ± 0.0011	−3.93	2.81
97% TFE[m]	0.0230 ± 0.0009	−3.30	2.83
90% TFE[m]	0.0598 ± 0.0019	−2.55	2.85
70% TFE[m]	0.611 ± 0.020	−1.98	2.96
50% TFE[m]	2.11 ± 0.04	−1.73	3.16
80T−20E	0.0623 ± 0.0029	−1.76	1.89
60T−40E	0.296 ± 0.005	−0.94	0.63
40T−60E	0.826 ± 0.009	−0.34	−0.48
20T−80E	1.42 ± 0.06	0.08	−1.42
97% HFIP[m]	0.155 ± 0.008	−5.26	5.17
90% HFIP[m]	0.101 ± 0.001	−3.84	4.31
70% HFIP[m]	0.444 ± 0.018	−2.94	3.83
50% HFIP[m]	1.37 ± 0.05	−2.49	3.80

[a] Substrate concentration of ca. 0.01 M in solvents containing fluoro alcohol and of 0.08 to 0.12 M in other solvents. [b] Unless otherwise indicated, binary solvents are on a volume−volume basis at 25.0 °C. [c] With associated standard deviation; average of all integrated first-order rate coefficients from duplicate runs. [d] From ref 19. [e] From refs 20 and 25. [f] Values of 2.50 (ref 8) and 2.11 (ref 10) at 25.0 °C. [g] Value of 12.1 at 25.0 °C (ref 10). [h] Value of 36.6 at 25.0 °C (ref 10). [i] Values of 36.3 and 38.7 at 25.0 °C (refs 7 and 10) and of 35.0 at 24.5 °C (ref 9). [j] Also value of 8.89 (± 0.07) at 25.0 °C and earlier values, at 25.0 °C, of 9.03 and 8.68 (refs 6 and 10). [k] Value of 0.940 at 25.0 °C (ref 10). [l] Extrapolation of values at 50.0−70.2 °C (ref 5) leads to a value of 0.269 for formic acid containing 1% by volume of H_2O at 24.2 °C. [m] On a weight−weight basis.

Table 2. Specific Rates of Solvolysis of Ethyl Chlorothioformate[a] at 25.0 °C and Comparison with Specific Rates of Solvolysis of Ethyl Chloroformate at 24.2 °C[b]

solvent[c]	$10^5\ k^{EtSCOCl}$, $s^{-1\ d}$	$k^{EtSCOCl}/k^{EtOCOCl}$
100% EtOH	0.43 ± 0.01[e]	0.19
90% EtOH	1.16 ± 0.01	0.21
80% EtOH	2.68 ± 0.02	0.37
60% EtOH	20.0 ± 0.5	1.65
100% MeOH	2.15 ± 0.03	0.26
80% MeOH	9.94 ± 0.09	0.40
60% MeOH	59.9 ± 0.6	1.49
80% acetone	0.48 ± 0.01	0.50
60% acetone	8.51 ± 0.07	2.31
100% TFE	4.92 ± 0.07	273
97% TFE	5.98 ± 0.07	260
90% TFE	10.2 ± 0.2	171
70% TFE	54.3 ± 0.5	89
50% TFE	194 ± 3	92
80T−20E	1.12 ± 0.02	18
60T−40E	0.46 ± 0.01	1.6
40T−60E	0.32 ± 0.01	0.39
97% HFIP	39.2 ± 1.8	253
90% HFIP	36.1 ± 0.7	357
70% HFIP	81.3 ± 0.8	183
50% HFIP	172 ± 5	126
100% H_2O	4980[f]	146[g]

[a] Concentration of 0.006−0.012 M. [b] From Table 1. [c] On volume−volume basis at 25.0 °C, except for TFE−H_2O and HFIP−H_2O mixtures, which are on a weight-weight basis. [d] With associated standard deviation; average of all integrated first-order rate coefficients from duplicate runs. [e] From the activation parameters given in ref 8, a value of 0.31 × 10^{-5} s^{-1} can be calculated (the reported specific rates of ethanolysis appear to be one order of magnitude too high). [f] Estimated from extrapolated value for methyl thiochloroformate at 25.0 °C and the Et/Me ratio at 4.6 °C (data from ref 24). [g] Using specific rates from ref 24, a value of 65 at 4.6 °C is obtained.

probability of 0.68 that the value is not statistically significant), a c value of −0.62 ± 1.06, a correlation coefficient of 0.073, and an F-test value of 0.18. Clearly, this equation does not correlate the data, and the negligible m value suggests that there is a general trend for the lN_T and mY_{Cl} terms to be of opposite sign and comparable magnitude.

The correlation is considerably improved by use of the full eq 2, with values of 1.00 ± 0.08 for l, 0.46 ± 0.05 for m and −0.07 ± 0.43 for c. The correlation coefficient (R) is still rather low at 0.918 and the F-test value is 86. Inspection of the data shows that six of the aqueous fluoro alcohol solvents lie above the plot, and the situation is reminiscent of that recently observed in a study of the specific rates of solvolysis of phenyl chlorothioformate,[23] where the aqueous TFE and aqueous HFIP data points were analyzed (in terms of eq 2) separately from the other solvents and two good correlations were obtained. These correlations led to l and m values consistent with one set resulting from an addition−elimination reaction channel and the other from an ionization channel involving appreciable nucleophilic solvation of the incipient acylium ion at the transition state (Table 3). The very good division, with only one of the studied solvents not being indicated to have at least 88% of the reaction by one or the other of the two reaction pathways, is a direct consequence of the two very different sets of l and m values associated with the two solvolysis mechanisms.

The division of the solvent systems between the two reaction channels is somewhat different for ethyl chloroformate in that only the 100% and 97% TFE−H_2O solvents are assigned to the ionization channel, and the 90−50% TFE−H_2O solvents are assigned to the addition−elimination channel. Also, consistent with the claim by Crunden and Hudson[5] that the ionization mechanism applies in formic acid, the specific rate of formolysis has been assigned to the ionization channel (formic acid was not included in the study of phenyl chlorothioformate solvolysis). This leads to a division of the 35 solvent systems for which both N_T and Y_{Cl} values are available into 28 which are assigned to the addition−elimination channel and 7 which are assigned to the ionization channel. The sensitivities and other correlation data obtained from the analyses in terms of eq 2 are reported, together with corresponding values for phenyl chloroformate[21] and phenyl chlorothioformate,[23] in Table 3. The correlations for each of the two reaction channels

Table 3. Correlation of the Specific Rates of Solvolysis of Phenyl and Ethyl Chloroformates and Chlorothioformates Using the Extended Grunwald−Winstein Equation

substrate	mechanism[a]	n[b]	l[c]	m[c]	c[c]	R[d]	F[e]
PhOCOCl	A−E	21[f]	1.68 ± 0.10	0.57 ± 0.06	0.12 ± 0.41	0.973	159
PhSCOCl	A−E	16[g]	1.74 ± 0.17	0.48 ± 0.07	0.19 ± 0.23	0.946	55
PhSCOCl	I	6[g]	0.62 ± 0.08	0.92 ± 0.11	−2.29 ± 0.13[h]	0.983	44
EtOCOCl	A−E	28[i]	1.56 ± 0.09	0.55 ± 0.03	0.19 ± 0.24	0.967	179
EtOCOCl	I	7[i]	0.69 ± 0.13	0.82 ± 0.16	−2.40 ± 0.27[h]	0.946	17
EtSCOCl	I	19[j]	0.66 ± 0.08	0.93 ± 0.07	−0.16 ± 0.31	0.961	96

[a] The two reaction channels are designated as addition−elimination (A−E) and ionization (I). [b] Number of solvent systems included in the correlation. [c] Using eq 2, with standard errors for l and m values and with the standard error of the estimate accompanying the c value. [d] Correlation coefficient. [e] F-test value. [f] All solvent systems (ref 21). [g] The 22 solvent systems divided into the six aqueous fluoro alcohol solvents and the remainder (ref 23). [h] Large negative value for c because the experimental k_0 value is not for this reaction channel. [i] The solvent systems divided into HCOOH, 100% and 97% TFE, and 97−50% HFIP (n = 7) and the remainder (n = 28). [j] The 22 solvent systems (Table 2) with omission of EtOH, 90% EtOH, and MeOH.

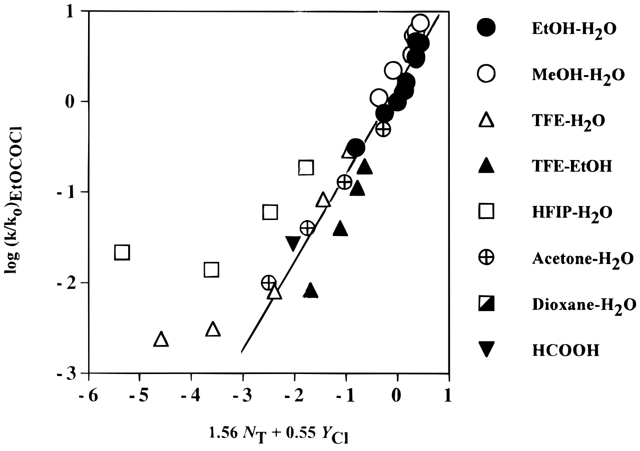

Figure 1. Plot of log(k/k_0) for solvolyses of ethyl chloroformate at 24.2 °C against ($1.56N_T + 0.55Y_{Cl}$). The data points for 100% and 97% TFE, HCOOH, and the HFIP−H_2O mixtures are not included in the correlation; they are added to show their considerable deviation from the correlation line.

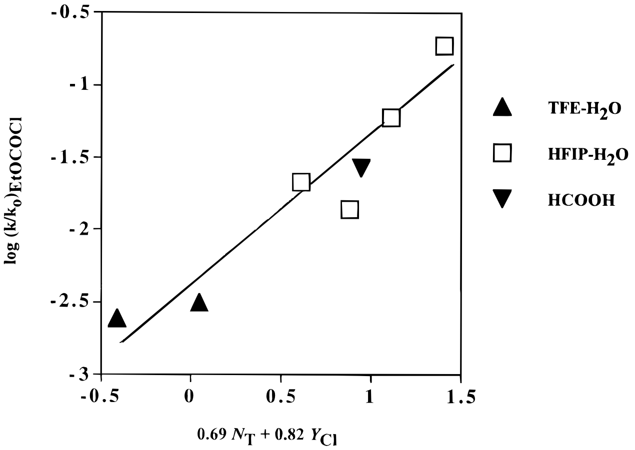

Figure 2. Plot of log(k/k_0) for solvolyses of ethyl chloroformate at 24.2 °C against ($0.69N_T + 0.82Y_{Cl}$).

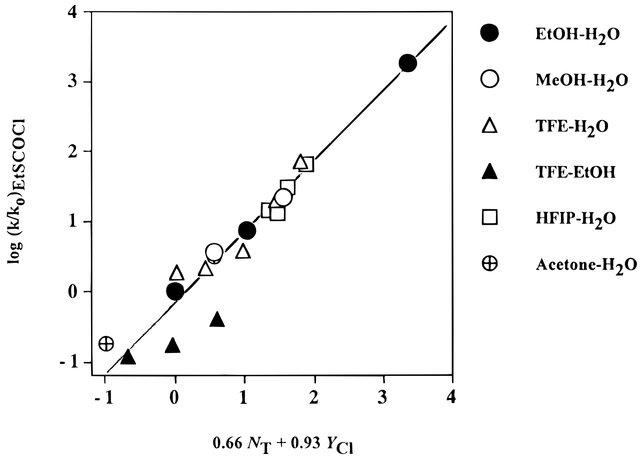

Figure 3. Plot of log(k/k_0) for solvolyses of ethyl chlorothioformate at 25.0 °C against ($0.66N_T + 0.93Y_{Cl}$) in the solvents of Table 2, with omission of EtOH, 90% EtOH, and MeOH.

for ethyl chloroformate solvolyses are presented graphically in Figures 1 and 2.

Also reported in Table 3 are values obtained from the analysis of the specific rates of solvolysis of ethyl chlorothioformate (Table 2). Included in this analysis is a data point for solvolysis in 100% water. The specific rate of hydrolysis is estimated from data presented by Queen[24] for methyl chlorothioformate at several temperatures and the Et/Me ratio as determined at 4.6 °C, with the assumption that this ratio can also be applied with reasonable accuracy at 25.0 °C. An analysis of the 22 specific rates of Table 2 gives, in terms of the simple Grunwald−Winstein equation, values of 0.40 ± 0.07 for m, −0.12 ± 0.66 for c, 0.792 for the correlation coefficient, and 34 for the F-test value. Again, the correlation is considerably improved, although still rather unsatisfactory, on use of the full eq 2, with values of 0.58 ± 0.11 for l, 0.76 ± 0.08 for m, 0.14 ± 0.42 for c, 0.926 for the correlation coefficient, and 57 for the F-test value. Application of these values shows that there are three systems, for the more nucleophilic and least ionizing solvents (100% ethanol, 90% ethanol, and 100% methanol), where the calculated specific rate value is less than 30% of the observed value. Excluding those values, we obtain the values presented in Table 3 and Figure 3: the l and m values are now essentially identical to those considered to reflect the ionization channel within the analyses of the solvolyses of phenyl chlorothioformate and ethyl chloroformate. Presumably, in the three excluded solvents, the addition−elimination channel is dominant; only three data points in similar solvents does not allow a correlation to be carried out. This assignment of mechanism for the solvolysis in ethanol is consistent with the finding by Orlov and co-workers[8] of very similar activation parameters for the ethanolyses of ethyl chloroformate and ethyl chlorothioformate, with, in particular, a very negative entropy of activation.

Inspection of the data of Table 3 provides strong evidence for the existence of the two proposed reaction channels. The first entry presents the l and m values associated with the unit mechanism operating for solvolysis of phenyl chloroformate[21] in all the solvents studied. The last entry shows the l and m values operating for the solvolysis of ethyl chlorothioformate in 19 of the 22 solvents studied, with the three omitted solvents being those of highest nucleophilicity and lowest ionizing power. The characteristics for the solvolyses of phenyl chlorothioformate[23] and ethyl chloroformate are intermediate, but both can be very well analyzed in terms of regions with the dominant operation of one of the two mechanisms, with a range of solvents for which the l and m values are extremely similar to those observed for phenyl chloroformate solvolysis and a further range, of the highly ionizing and low nucleophilicity solvents, where the l and m values are extremely similar to those observed for ethyl chlorothioformate solvolysis.

The ratios of the specific rates of ethyl chlorothioformate solvolysis relative to ethyl chloroformate solvolysis (values from Table 1 and Table 2) show a widely varying value for the ratio. In the three solvents assigned to the addition−elimination channel, the value is in the range of 0.19−0.26, consistent with the more electronegative oxygen resulting in a more electron-deficient center at the adjacent carbonyl carbon. The value then rises as one increases the water content of binary mixtures with ethanol, methanol, or acetone, or the TFE content of TFE−ethanol mixtures. For 100% water, aqueous TFE, and aqueous HFIP, values for the ratio are in the range of 89−357, reflecting that the higher electronegativity of the oxygen becomes unfavorable when the mechanism involves ionization. Previously,[24] in a comparison of chloroformate ester and chlorothioformate ester solvolyses by the ionization mechanism, it was assumed that sulfur would have a smaller tendency to use its electrons in a stabilizing interaction with the adjacent electron-deficient carbon of an incipient carbocation. We have not considered this effect to be a relevant factor in the comparison because recent high-level calculations have indicated that sulfur and oxygen have very similar abilities to donate lone-pair electrons to an adjacent carbocationic center.[26]

Prior to this study, formic acid was the only solvent within which it was believed[5] that the solvolysis of ethyl chloroformate followed an ionization pathway. Before the introduction of fluoro alcohols as reaction media, formic acid was usually the solvent of choice for favoring unimolecular over bimolecular nucleophilic substitution reactions.[27] Even in formic acid, it was found[5] that the introduction of more than 4% (volume−volume) water led to the incursion of a bimolecular pathway, suggesting that the formolysis is probably only marginally on the ionization mechanism side of the borderline region. This can be confirmed by calculation, using the data for the two reaction channels (Table 3) within eq 2. It is found that the overall calculated specific rate of formolysis involves an appreciable 29% contribution from the addition−elimination channel, accompanied by a dominant 71% contribution from the ionization channel.

Conclusions

Except for solvolyses in solvents which are highly ionizing and weakly nucleophilic, ethyl chloroformate solvolyzes by a reaction channel which, in terms of the extended Grunwald−Winstein equation (eq 2), gives values for l of 1.56 and for m of 0.55. These values are essential identical to values previously observed[21] for the solvolyses of phenyl chloroformate ($l = 1.68$; $m = 0.57$), solvolyses which are believed to proceed by an addition−elimination pathway over the full range of solvents usually employed in this type of study. Consistent with this assignment are the Cl/F ratios of unity or lower for solvolyses of ethyl halogenoformates, and also for solvolyses of aryl esters,[28] the relatively high k_{H_2O}/k_{D_2O} solvent isotope effects, and the large negative values for the entropies of activation.

For solvolyses in formic acid, 100% and 97% TFE and 97-50% HFIP, a reaction channel believed to involve ionization accompanied by a fairly strong nucleophilic solvation of the developing acylium ion ($l = 0.69$; $m = 0.82$) has been found to be dominant. The sensitivity values obtained for this pathway are very similar to those observed both for phenyl chlorothioformate in similar solvents[23] ($l = 0.62$; $m = 0.92$) and for ethyl chlorothioformate in all but the more nucleophilic and least ionizing solvents ($l = 0.66$; $m = 0.93$). Indeed, for ethyl chlorothioformate, the addition−elimination channel is believed to be dominant only in ethanol, 90% ethanol, and methanol.

Consistent with an assignment to the ionization reaction channel, the specific rates of formolysis of ethyl chloroformate in the 50−70 °C range[5] lead to a calculated entropy of activation of −2.6 eu, a value some 15−30 eu more positive than those observed for solvolyses proceeding by the addition−elimination channel.

We have found no evidence for an S_N2-type attack of solvent on either chloroformate or chlorothioformate esters. An S_N2 attack was recently proposed by Bentley and co-workers[14] for the solvolyses of acetyl chloride ($l = 0.86$; $m = 0.68$), and such an attack is nicely consistent with the large Cl/F rate ratios for solvolyses of simple acyl halides in binary solvent systems containing an alcohol or water.[16] The insertion of an electron-withdrawing oxygen or sulfur atom adjacent to the carbonyl carbon reaction center will assist nucleophilic attack and hinder carbon−halogen bond heterolysis, thereby favoring a rate-determining addition within an addition−elimination channel in its competition with a direct nucleophilic substitution channel.

Experimental Section

Ethyl chloroformate (Aldrich, 97%) was further purified by fractional distillation immediately prior to use. Ethyl chlorothioformate (Schweizerhall, 98%) was used without further purification. Solvents were purified and the kinetic runs carried out as previously described.[18] The multiple regression analyses were performed using the ABSTAT statistical package (Anderson-Bell, Arvada, CO).

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