Correlation of the Rates of Solvolysis of Benzoyl Fluoride and a Consideration of Leaving-Group Effects

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The specific rates of solvolysis of benzoyl fluoride have been determined at 25.0 °C in 37 pure and binary solvents. Together with seven values from the literature, these give a satisfactory correlation over the full range of solvents when the extended Grunwald−Winstein equation is applied. The sensitivities to changes in solvent nucleophilicity and solvent ionizing power are very similar to those for octyl fluoroformate, suggesting that the addition step of an addition−elimination mechanism is rate determining. In the solvent-composition region where benzoyl chloride also shows bimolecular solvolysis, the appreciable k_{Cl}/k_F values are proposed as being primarily due to a more efficient ground-state stabilization for the fluoride.

Benzoyl fluoride was the third compound with a carbon−fluorine bond to be synthesized[1] and the first to be prepared by the halide-exchange route.[2] It has been the subject of several kinetic investigations, mainly involving solvolysis[3−8] or aminolysis.[9−14] The solvolyses (eq 1) are subject to catalysis by added strong acids and, with relatively high substrate concentrations, autocatalysis has also been observed. Since these acid catalysis effects are not observed with other benzoyl halides, it is usually proposed[6,7,15,16] that the protonation occurs on fluorine, giving assistance to the breaking of the carbon−fluorine bond in the rate-determining step. A parallel explanation was proposed[17] for the acid catalysis of the hydrolysis of acetyl fluoride.

$$C_6H_5COF \xrightarrow{H_2O/ROH} C_6H_5COOH + C_6H_5COOR + HF \qquad (1)$$

Solvolyses of *p*-(dimethylamino)benzoyl fluoride were established,[8] in highly ionizing and/or low nucleophilicity solvents, as proceeding by a mechanism involving ionization to an acylium ion in the rate-determining step, followed by its relatively rapid capture. For the parent benzoyl chloride and ring-substituted derivatives without highly electron-supplying substituents, a pathway involving nucleophilic attack on substrate has usually been proposed. Several of the earlier reports[3,4,6a,16] are a little vague as regards mechanism but appear to favor a concerted process, largely on the basis of large k_{Cl}/k_F ratios. Bender and Jones[9] pointed out that the large values can be rationalized in terms of a tetrahedral intermediate that returns to reactants much more often than it proceeds to products, such that the fission of the carbon−fluorine bond will be rate determining. Several subsequent reports have given support to a mechanism of this general type.[6b,10,13] Other workers have considered the mechanism to be near the borderline between concerted and stepwise and, therefore, difficult to define.[8,11,12,14,15] Jencks and Song favored, for aminolysis,[12] a concerted pathway, involving characteristics of addition, without a stepwise mechanism being rigorously excluded and, for solvolysis,[8] an uncoupled concerted pathway.

A recent report[18] concerning the solvolyses of octyl fluoroformate and chloroformate found the k_{Cl}/k_F ratio to be only slightly greater than unity in 100% ethanol and

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100% methanol and to be somewhat below 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 association step of an association−dissociation mechanism being rate determining. Similar results and conclusions had been reported earlier for ethyl haloformate[19,20] and aryl haloformate[21] solvolyses. In contrast, as mentioned above, for both solvolyses and aminolyses of benzoyl halides and, especially, acetyl halides, it has usually been found that the chloride reacts considerably faster than the fluoride[7,8,10,12,15−17,22] and this has usually been rationalized either in terms of a concerted process or an association−dissociation pathway with dissociation being rate determining.

The extended Grunwald−Winstein equation (eq 2) treatment of octyl fluoroformate solvolysis led to a value

$$\log(k/k_0) = lN_T + mY_{Cl} + c \qquad (2)$$

for l, representing the sensitivity to changes in solvent nucleophilicity (N_T),[23,24] of 1.67 ± 0.07 and for m, representing the sensitivity to changes in solvent ionizing power (Y_{Cl}),[25,26] of 0.76 ± 0.03. These values were found[18] to be similar to those for a variety of chloroformate esters believed to solvolyze by the association−dissociation pathway with association being rate determining. The other entities in eq 2 are k and k_0 representing, respectively, the specific rates of solvolysis in a given solvent and in 80% ethanol, and c, a constant (residual) term.

One might question the use of Y_{Cl} for solvolyses of a fluoride, but Y_F values are not available and, in the absence of acid catalysis, 1-adamantyl fluoride (with the recommended[25,26] 1-adamantyl component for poor leaving groups) would solvolyze prohibitively slowly.[27] However, for acid chlorides, if association is rate determining, the solvent influence is for the movement of the electrons within the carbonyl group toward the oxygen. Fortunately, Y_{Cl} appears to be a reasonable scale for this process. Since this process will be essentially identical for association of solvent with fluoroformates, one would expect the Y_{Cl} scale to also be a reasonable choice for solvolyses of fluoroformates and acyl fluorides.

A recent analysis using eq 2 of data available for solvolyses of benzoyl chloride and four para-substituted derivatives[28] indicated an ionization pathway over the full range of solvents for the *p*-methoxy derivative and an addition−elimination pathway for all but 97% 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) for the *p*-nitro derivative. The parent compound, the *p*-methyl derivative, and the *p*-chloro derivative solvolyzed by either (or both) of the mechanisms depending upon the properties of the solvent. In particular, for the parent benzoyl chloride, the mechanistic switch in binary aqueous solvents was at approximately 70% methanol, 60% ethanol, and 50% acetone. For TFE−ethanol mixtures, it was at about 70% TFE content.

The duality of mechanism for benzoyl chloride leads to the need to exercise caution in the interpretation of k_{Cl}/k_F ratios for benzoyl halide solvolyses, since, for a given solvent, the two halides may not be solvolyzing by an identical pathway. Kinetic data recently became available[29] for the solvolyses of benzoyl bromide and three para-substituted derivatives in a variety of solvents. These data allow an extension of the consideration of leaving group effects to a bromide ion leaving group.

In the present study, we consider the solvent variation of the specific rates of solvolysis of benzoyl fluoride in terms of linear free energy relationships (LFER) and these analyses are then combined with a consideration of leaving-group effects to arrive at a reasonable mechanism.

Results

The specific rates of solvolysis of benzoyl fluoride at 25.0 °C are reported in Table 1. Of the values reported in the table, 37 are determined in this study and 7 are abstracted from reports[5,8] of earlier determinations. Of the total of 44 solvents used in the solvolysis studies, N_T[23,24] and Y_{Cl}[25,26] values were both available for 41 solvents and these were utilized in the extended Grunwald−Winstein treatment using eq 2. The required Y_{Cl} values were not available for three of the aqueous dioxane compositions used for the benzoyl fluoride solvolyses. The N_T and Y_{Cl} values are reported in Table 1, as are k_{Cl}/k_F ratios determined using available literature values[5,8,30−35] for the specific rates of solvolysis of benzoyl chloride at 25.0 °C.

Discussion

The observation of k_{Cl}/k_F ratios of at least 38 (Table 1) has to be reconciled with the values of close to unity, frequently slightly below unity, observed for solvolyses of haloformate esters.[18−21] This variance has suggested[36] differences in mechanism and a useful additional probe will be to apply the extended Grunwald−Winstein equa-

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TABLE 1. Specific Rates of Solvolysis of Benzoyl Fluoride[a] in a Variety of Pure and Mixed Solvents at 25.0 °C, the N_T and Y_{Cl} Values for the Solvents, and a Comparison with Corresponding Values for Solvolysis of Benzoyl Chloride (k_{Cl}/k_F)

solvent[b]	$10^5 k_F$/s^{-1} [c]	N_T[d]	Y_{Cl}[e]	(k_{Cl}/k_F)
100% EtOH	0.148 ± 0.006[f]	0.37	−2.52	524;[g] 466[h]
90% EtOH	3.16 ± 0.09	0.16	−0.94	52[h]
80% EtOH	6.53 ± 0.18[f]	0.00	0.00	42;[g] 45[h]
70% EtOH	9.95 ± 0.11	−0.20	0.78	45[h]
60% EtOH	15.6 ± 0.5	−0.38	1.38	55[h]
50% EtOH	25.5 ± 1.5	−0.58	2.02	71[h]
40% EtOH	41.6 ± 1.3[f]	−0.74	2.75	128;[g] 123[i]
20% EtOH	110 ± 6	−1.16	4.09	336[i]
100% H_2O	180[j,k]	−1.38	4.57	611[j]
100% MeOH	1.23 ± 0.10	0.17	−1.17	347[h]
96.7% MeOH	3.63[f]	0.12[l]	−0.81[l]	151[g]
90% MeOH	13.0 ± 0.9	−0.01	−0.18	62[h]
80% MeOH	25.6 ± 1.2	−0.06	0.67	50[h]
70% MeOH	45.7 ± 1.4	−0.40	1.46	44[h]
69.5% MeOH	42.7[f]	−0.40[l]	1.50[l]	45[g]
60% MeOH	71.1 ± 1.8	−0.54	2.07	49[h]
40% MeOH	138 ± 6	−0.87	3.25	97[i]
20% MeOH	160 ± 7	−1.23	4.10	338[i]
95% acetone	7.98 (± 0.08) × 10^{-3}	−0.49	−3.19	687[m]
90% acetone	0.0586 ± 0.0011	−0.35	−2.22	293[n]
80% acetone	0.409 ± 0.011[f]	−0.37	−0.83	123;[g] 164[h]
70% acetone	1.32[f]	−0.42	0.17	83[g]
60% acetone	5.58 ± 0.13	−0.52	0.95	46;[h] 45[m]
50% acetone	7.95[f]	−0.70	1.73	102[g]
40% acetone	16.2 ± 0.5	−0.83	2.46	154[i]
20% acetone	69.6 ± 1.3	−1.11	3.77	359[i]
80% dioxane	0.524 ± 0.018	−0.46		107[o]
60% dioxane	6.84 ± 0.10	−0.54		38
40% dioxane	19.3 ± 0.8	−0.84		108
20% dioxane	77.3 ± 1.3	−1.12	3.71	258
97% TFE[p]	0.00117[q]	−3.30	2.83	311 × 10^3 [i]
90% TFE[p]	0.103 ± 0.001	−2.55	2.85	5.46 × 10^3 [i]
80% TFE[p]	0.484 ± 0.028	−2.19	2.90	2.32 × 10^3 [i]
70% TFE[p]	1.53 ± 0.09	−1.98	2.96	1.28 × 10^3 [i]
50% TFE[p]	6.55 ± 0.20	−1.73	3.16	831[i]
80T−20E[r]	0.0236 ± 0.0013	−1.76	1.89	4.65 × 10^3 [h]
60T−40E[r]	0.0547 ± 0.0011	−0.94	0.63	1.76 × 10^3 [h]
40T−60E[r]	0.102 ± 0.005	−0.34	−0.48	648;[h] 593[s]
20T−80E[r]	0.125 ± 0.011	0.08	−1.42	576[s]
90% HFIP[p]	0.0269 ± 0.0017	−3.84	4.31	
70% HFIP[p]	1.43 ± 0.10	−2.94	3.83	
50% HFIP[p]	5.21 ± 0.16	−2.49	3.80	
AcOH	0.000209[f]	−1.78	−1.60	5.01 × 10^3 [g]
HCO_2H	0.151[f]	−2.44	3.20	13 × 10^3 [t]

[a] Substrate concentration of 0.010 mol dm^{-3}, unless otherwise indicated. [b] Unless otherwise indicated, the binary solvents are on a volume−volume basis at 25.0 °C, with the other component being water. [c] With associated standard deviations; average of all integrated first-order rate coefficients from duplicate runs. [d] From refs 23 and 24. [e] From refs 25 and 26. [f] From ref 5: values of 0.162 in 100% EtOH, 6.17 in 80% EtOH, 39.8 in 40% EtOH, and 0.398 in 80% acetone; six additional values are presented in the table. [g] Using the values from ref 5. [h] Value for benzoyl chloride from ref 30. [i] Value for benzoyl chloride (interpolated for 90% TFE and 80% TFE) from ref 31. [j] Values from ref 8. [k] A solvent deuterium isotope effect value (k_H/k_D) of 2.0 (ref 8). [l] Interpolated value. [m] Value for benzoyl chloride from ref 32. [n] Value for benzoyl chloride from ref 5. [o] Value for benzoyl chloride by interpolation within data of ref 33. [p] On a weight/weight basis; substrate concentration 0.020 mol dm^{-3}. [q] Extrapolated value based on $10^7 k$ (s^{-1}) values of 64.9 ± 2.2 at 82.4 °C, 7.64 ± 0.21 at 62.4 °C, and 2.56 ± 0.20 at 50.0 °C. [r] T−E are TFE−ethanol mixtures; substrate concentration 0.020 mol dm^{-3}. [s] Value for benzoyl chloride from ref 34. [t] Value for benzoyl chloride (ref 31b) approximately extrapolated from data at 9 °C (ref 35).

tion (eq 2) and compare the *l* and *m* values with those previously obtained for octyl fluoroformate. A more direct comparison can also be made by constructing the LFER for a direct comparison of benzoyl fluoride and octyl fluoroformate specific rates of solvolysis in a series of solvents.

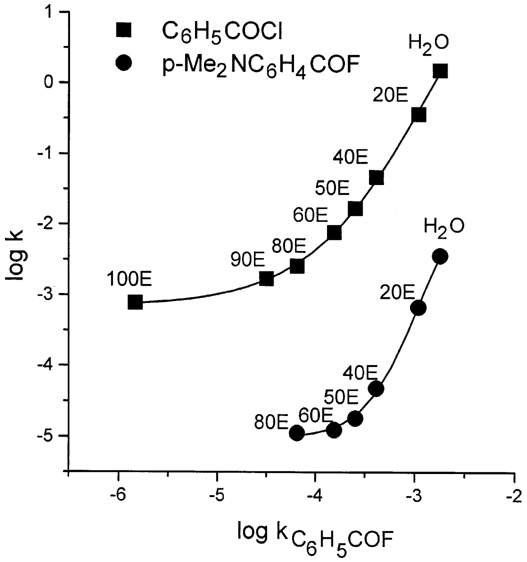

FIGURE 1. Logarithmic plots of the specific rates of solvolysis of benzoyl chloride and *p*-(dimethylamino)benzoyl fluoride against the specific rates of solvolysis of benzoyl fluoride for aqueous−ethanol compositions at 25.0 °C.

The treatment in terms of the extended Grunwald−Winstein equation leads to values of 1.58 ± 0.09 for *l*, 0.82 ± 0.05 for *m*, and −0.09 for *c*. The multiple correlation coefficient (*R*) is 0.953, the *F*-test value is 186, and the standard error of the estimate is 0.10. The plot is not shown. The *l* and *m* values are very similar to those for octyl fluoroformate.[18] For the 26 solvents for which specific rates are available for both benzoyl fluoride and octyl fluoroformate, a direct comparison through an LFER plot leads to good linearity with a slope of 0.95 ± 0.05, intercept of 0.06 ± 0.07, correlation coefficient of 0.966, and *F*-test value of 338.

Since octyl fluoroformate is believed to solvolyze by an addition−elimination pathway in all of the solvents involved in the plots, the similarity in *l* and *m* values for the two solvolyses, coupled with the good direct LFER plot, gives rather strong evidence for an association−dissociation mechanism.

Solvolyses for which a unit mechanism is observed over a wide range of solvents can be useful as a standard for an LFER investigation of possible solvent-induced changes in mechanism in other solvolyses.[31a] For example, the solvolyses of *p*-methoxybenzoyl[28,31a] and *p*-nitrobenzoyl[28] chlorides have been used in this way. We can also consider the possible use of the solvolyses of benzoyl fluoride as a similarity model.

A plot of log *k* for benzoyl chloride solvolysis against log *k* for benzoyl fluoride solvolysis is shown in Figure 1. The previously determined aqueous−ethanol solvent range for a dominant ionization mechanism for benzoyl chloride solvolysis, with more than 60% water content,[28] gives a linear plot with a slope of 2.27 (correlation coefficient of 0.9978). The points for the less-aqueous solvents lie above the plot, considerably above for 100−80% ethanol, consistent with the previously indicated incursion of an appreciable contribution from the addition−elimination pathway. However, a good linear relationship is not observed in the bimolecular range, associated with the appreciably higher *m* value for benzoyl fluoride solvolyses when eq 2 is applied. Indeed, the different responses to changes in solvent ionizing power suggest that benzoyl fluoride solvolysis will not be a good similarity model for the bimolecular acyl chloride solvolyses.

An LFER comparison with other acyl fluorides could be more fruitful and the solvolyses of *p*-(dimethylamino)-benzoyl fluoride, previously studied in aqueous ethanol and plotted against Y_{Cl},[8] can alternatively be plotted against log *k* for benzoyl fluoride solvolyses; this plot is also shown in Figure 1. As with the benzoyl chloride plot, a good linear plot (correlation coefficient of 0.9984 and slope of 2.92) is observed at high water content. It starts to curve upward at beyond 40% EtOH, at slightly lower ethanol content than for benzoyl chloride (which is linear as far as 50% ethanol content). The plots are consistent with both of the solvolyses which are compared to the solvolyses of benzoyl fluoride in Figure 1 undergoing a solvent-induced change in mechanism. Since the solvolyses of *p*-(dimethylamino)benzoyl fluoride were studied only as far as 80% ethanol,[8] the solvent range for the bimolecular mechanism is insufficient for a correlation analysis in this region to be possible. The slopes of greater than unity for the linear regions of both plots are consistent with the expected[8,28] wider variation of specific rate for the unimolecular mechanism involved in this region relative to the corresponding bimolecular solvolyses of benzoyl fluoride.

In the comparison of $k_{\mathrm{Cl}}/k_{\mathrm{F}}$ ratios for benzoyl chloride and benzoyl fluoride, one must bear in mind that, for the solvolyses of the chloride previously shown to proceed by an ionization mechanism,[28] the corresponding fluoride would react *much* slower by this mechanism and the bimolecular mechanism (probably with general-base catalysis[8,37,38]) will be the one in operation. For example, for the hydrolyses in 100% H_2O of the *p*-(dimethylamino)-benzoyl halides, the $k_{\mathrm{Cl}}/k_{\mathrm{F}}$ ratio[8] is very large (3×10^7). Accordingly, the appreciable but somewhat lower values observed in TFE−H_2O, TFE−EtOH, acetic acid, and formic acid, the largest being 3.1×10^5 for solvolysis in 97% TFE, can be considered to reflect a comparison of ionization reaction of benzoyl chloride with bimolecular reaction of benzoyl fluoride.

The value of 38 observed in 60% dioxane changes only slightly as one replaces the dioxane component with ethanol, methanol, or acetone. For all four of these binary systems, the $k_{\mathrm{Cl}}/k_{\mathrm{F}}$ value initially falls from the value in the pure solvents or in solvents with an appreciable organic component as increasing amounts of water are present and then when the water content starts to move above 40%, with increasing tendency toward ionization reaction for the benzoyl chloride solvolysis,[28] the trend reverses as the values start to rise, culminating in a value of 611 at 100% H_2O. Our interest in the $k_{\mathrm{Cl}}/k_{\mathrm{F}}$ ratio is primarily concentrated in the less aqueous region where both of the halides react by the bimolecular mechanism and with the observation that, unlike for haloformate ester solvolysis, the ratio does not fall to unity (or slightly lower).

When both of the halides are reacting by the same mechanism, the $k_{\mathrm{Cl}}/k_{\mathrm{F}}$ ratio is usually taken as a measure of the extent of bond breaking in the C−X bond at the transition state of the rate-determining step.[4] Application of this argument to the bimolecular solvolysis would require either a concerted displacement pathway or a rate-determining role for the second step of an addition−elimination pathway. This type of argument was used by Swain and Scott[4,39] in a consideration of RCl/RF ratios for solvolyses in aqueous acetone. A range of values from 10^6 for triphenylmethyl halides to 10^2 for benzoyl halides was observed and the results discussed in terms of the relative amounts of C−X bond fission and C−O bond formation at the transition state.

An interesting result was that, for reaction of benzoyl halides with hydroxide ion in 50% acetone, the $k_{\mathrm{Cl}}/k_{\mathrm{F}}$ ratio for the second-order rate coefficients was somewhat below unity (0.71).[4] However, values of unity or lower are not always a feature of reactions under nonsolvolytic conditions. Bender and Jones[9] found extremely large leaving-group effects in a consideration of the second-order rate coefficients for the reaction of benzoyl halides with morpholine in cyclohexane as solvent. The $k_{\mathrm{Cl}}/k_{\mathrm{F}}$ ratio was 2600 and the $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ ratio was 25. The overall ratio ($k_{\mathrm{I}}/k_{\mathrm{F}}$) was about 10^5. The authors proposed two ways by which the rather large rate differences could occur. One involves the partitioning of the intermediate needing consideration, with a considerable return to reactants being able to compete effectively with progress to products. The other involved a ground-state effect with differences in the efficiency of resonance stabilization of the reactant. They concluded that both effects were of importance but that data did not allow an assessment of the relative importance of the two effects.

There has been a consideration of the stabilization by bromine and chlorine of a carbon−carbon double bond. Application of ab initio MO calculations indicated that the stabilization by chlorine was greater by 1.3 kcal/mol. It was pointed out that this could translate into a factor of about 10-fold in reactivity and modest values of about this magnitude could be observed even if the addition step was rate determining.[40] A subsequent theoretical study[41] confirmed that substituent effects at the vinyl carbon are modest and it was emphasized that they are much less than at the acetyl carbon. For the acetyl carbon the detailed nature of the interaction depends on the nature of the substituent but calculation indicates that there can be strong Coulombic interactions, due to the very pronounced polarization of the carbonyl group.[42]

A theoretical evaluation of the effects of fluorine in acetyl fluoride[42] indicated a relatively small effect from π-electron donation and a major contribution resulting from the high polarity in the C−F bond, which Coulombically stabilizes the C−O group, such that both the C−X[43] and C−O bonds are strengthened by the introduction of a more electronegative substituent. This results

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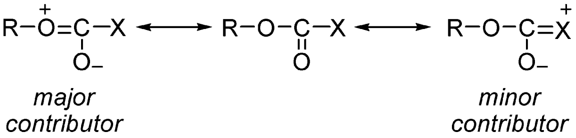
in larger effects for CH_3COX than for CH_3X or $CH_2{=}CHX$.[41,42] It was proposed[44] that fluorine will act as a π-electron donor only when a full positive charge can be stabilized. It was also shown[42] that chlorine is a rather poor π-electron donor. While the calculations suggest that Bender and Jones could well be correct in their assumption of an important ground-state stabilization, their description of it as a resonance stabilization would seem to imply π-electron donation, whereas the major influence indicated by calculation is Coulombic in origin.

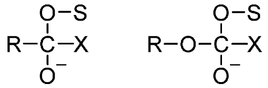
While differences in ground-state stabilization could explain appreciable k_{Cl}/k_F ratios for solvolyses of acyl halides even if addition is rate determining, it is still necessary to rationalize why large values can be observed for the simple acyl halides (RCOCl, with R being alkyl or aryl) but haloformate solvolyses usually show a k_{Cl}/k_F ratio of close to unity. In this connection, it can be noted that haloformate solvolyses are appreciably slower than those of the related acyl halide with the non-carbonyl oxygen removed. For example, for solvolyses in 89.1% acetone at 25.0 °C, acetyl chloride reacts 9×10^3 times faster than methyl chloroformate.[45] This is usually rationalized in terms of ground-state stabilization, involving π-electron donation from the oxygen.[36] It is reasonable to suppose that a strong effect of this nature could outweigh the alternative of stabilizing influences involving the halogen, which is only a weak π-electron donor and where the Coulombic influence will be reduced by the interaction of the oxygen with the positive charge of the α-carbon. This situation, expressed in terms of π-electron donation, is illustrated in eq 3.



$$R-\overset{+}{O}=\underset{O^-}{C}-X \longleftrightarrow R-O-\underset{\overset{\|}{O}}{C}-X \longleftrightarrow R-O-\underset{O^-}{C}=\overset{+}{X} \quad (3)$$

The possibility that the relatively large k_{Cl}/k_F rate ratios for bimolecular attack arise from an increase in return to reactants for the fluoride (stronger C$-$X bond) relative to that for the chlorides[9] must also be considered. It is reasonable that such return would be more appreciable for an acyl halide than for a haloformate ester. If we assume deprotonation through general-base catalysis in reaction with either alcohol or water (SOH), then the intermediates can be written as in Scheme 1. These formulations assume that the negatively charged oxygen is not appreciably protonated. Either way, both types of intermediate would have a considerable driving force for ejection of a halide ion, as is indicated by the 10^9 difference in solvolysis rates for ethoxymethyl chloride and butyl chloride, a minimum value for the influence of the ethoxy group on ionization rates.[46] The presence of the additional alkoxy (or aryloxy) group in the intermediate from the haloformate ester would give an additional driving force to the large driving force already present in the intermediate from the acyl halide. There is evidence from ^{18}O exchange for return to reactants from intermediate during hydrolysis of benzoyl chloride in 67$-$75% acetone.[47] The amount is relatively small, however, suggesting that only one in 19$-$26 intermediates returns to reactant. This would result in only a minor perturbation of the concept that the association step is rate determining.

SCHEME 1



$$R-\underset{O^-}{\overset{O-S}{C}}-X \qquad R-O-\underset{O^-}{\overset{O-S}{C}}-X$$

Since k_{Cl}/k_F rate ratios for S_N1 solvolyses have been found to be in the range of 10^6 (for Ph_3CX[39]) to 10^7 (for p-$Me_2NC_6H_4COX$[8]), the relatively slow loss of fluoride could lead to a situation where, for the fluoride, return to reactant could be competitive for acyl fluorides but not for acyl chlorides or haloformate esters. If partitioning was important for benzoyl fluoride but not for octyl fluoroformate, then one would expect this to be reflected in the l and m values determined with eq 2. Changes would be expected if the rate-determining step changes, at least partially, from formation of the intermediate to its progression to products. As already mentioned, the differences in sensitivity values for the solvolyses of the two substrates are very minor. This would suggest that, if partitioning was important for the fluoride, the ratio of return to product formation would have to be largely independent of the identity of the solvent. This seems rather unlikely since the fission of the C$-$F bond is generally considered to be strongly influenced by the solvation of the incipient fluoride ion.[9,15] It appears that the important characteristics of benzoyl fluoride solvolysis, including the comparison with octyl fluoroformate solvolysis, are best explained in terms of an addition$-$elimination pathway, with fairly large k_{Cl}/k_F ratios resulting from ground-state stabilization, especially important for the fluoride. It is not possible, however, to completely rule out influences from a possible return to reactant from the tetrahedral intermediate.

The consideration of leaving-group effects can be extended to benzoyl bromide by using a report by Liu and Hou[29] of the rates of solvolysis at 25.0 °C. High reactivity at 25 °C and low solubility of substrate at lower temperatures limited the range of solvent composition to no more than 30% water content in binary mixtures with ethanol, methanol, and acetone. The k_{Br}/k_{Cl} ratios, in a comparison with benzoyl chloride solvolysis rates,[28,30] show only a moderate variation with solvent composition. The solvolyses in the above-mentioned binary mixtures are to be expected to be bimolecular in character and in 100$-$80% methanol the ratio was 24$-$30 and the value rose to 74$-$86 in 80$-$70% acetone. A value of 86 in 100% ethanol fell to 43 in 90% ethanol and to 29 in 80% ethanol. In 100% TFE, the mechanism will involve rate-determining ionization, but the value of 34 remains in the same range, with a slight increase to 57$-$71 in TFE$-$ethanol mixtures with 20$-$60% ethanol content. It does not appear that for these solvolyses the k_{Br}/k_{Cl} value could be helpful in assigning mechanism. The magnitudes of the values for the ratio are consistent with values previously tabulated for reactions of aliphatic[48] and aromatic[49] acyl halides.

In considering the k_{Br}/k_{Cl} ratio, it is possible to show that the ratio is not only rather insensitive to changing

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TABLE 2. Comparison of k_{Cl}/k_F Ratios for *p*-Methylbenzoyl Halide, Benzoyl Halide, and *p*-Nitrobenzoyl Halide Solvolyses[a] at 25.0 °C

solvent	k_{Cl}/k_F		
	p-MeC_6H_4COX	C_6H_5COX	*p*-$NO_2C_6H_4COX$
100% EtOH		524	79
80% EtOH	162	42	4.9
40% EtOH		128	2.5
100% H_2O		611[b]	1.2[b]
100% MeOH		347	158
80% acetone	276	123	17.4
70% acetone		83	9.6
50% acetone	932	102	4.1
AcOH	10.9×10^3	5.01×10^3	246
HCO_2H		13×10^3	37.2

[a] Specific rate values from ref 5, unless otherwise stated. [b] From ref 8.

the solvent, it is also only modestly changed by the introduction of a para substituent into the two substrates.[28-30] With electron-supplying substituents, the ratio range for the parents (24−86) rises slightly to 42−130 on introduction of a *p*-methyl group and this value continues to rise modestly on changing to a *p*-methoxy group (58−135). Introduction of the moderately electron-withdrawing *p*-chloro substituent leaves the range of values essentially unchanged (20−81).

The effect of para substituents upon the k_{Cl}/k_F ratio for two substituents and for the parent benzoyl halides (parent data also in Table 1) is shown in Table 2. Except for the solvolyses in 100% H_2O,[8] the data are from a study by Swain, Mosely, and Bown.[5] Large k_{Cl}/k_F values are obtained for solvolyses of the *p*-methyl derivative because the solvents are ones where the chloride would be solvolyzing by the ionization mechanism. For the solvolyses of *p*-nitrobenzoyl chloride all of the solvolyses, chloride and fluoride, will be by the bimolecular mechanism.[28] The values are uniformly smaller than those for the solvolyses of benzoyl halides and in 100% water a value of only 1.2 is obtained. This is consistent with a considerable ground-state solvation of the fluorine, with partial transfer of negative charge to solvent molecules such that the stabilizing intramolecular Coulombic forces are reduced. This approach predicts the fall in k_{Cl}/k_F value as one proceeds from 100% ethanol to 100% water. A similar trend is observed for the parent benzoyl halides, except with more than 30% water (40% for aqueous acetone) the trend reverses itself because of the introduction of the ionization mechanism for benzoyl chloride.[28]

An interesting aspect of acyl halide solvolyses is that only the fluorides are subject to acid catalysis.[3,6,7,15-17] This was very reasonably taken as evidence for protonation at the fluorine because protonation at the carbonyl oxygen would be expected to have similar consequences for all acyl halides. Further consideration is then usually in terms of the protonation assisting the rupture of the C−F bond. If one is arguing against this bond being broken, because the addition step is rate determining, then it must be assumed either that the protonation leads to a change in reaction mechanism, such as to an ionization mechanism, which is certainly possible, or some other factor is responsible for increasing the rate of reaction of the protonated acyl fluorides. Indeed, such an effect is to be expected if Coulombic interactions are an important influence in the determination of k_{Cl}/k_F rate ratios. After protonation, the fluorine will carry a positive, not a negative charge and calculations[42] support what one would intuitively predict that placing a positive charge next to the positive charge of the carbonyl carbon has a large destabilizing ground-state effect, which can lead to appreciably faster reactions. Indeed, the influence of protonation can be considered as a logical extension of the reduction in Coulombic stabilization, due to very efficient hydrogen bonding, as the water content of mixed solvents is increased.

Conclusions

The solvolyses of benzoyl fluoride give a satisfactory extended Grunwald−Winstein correlation (eq 2) over a wide range of N_T and Y_{Cl} values, from 100% ethanol (tending to favor bimolecular solvolysis) to 90% HFIP (tending to favor ionization pathways). The sensitivities to changes in N_T and Y_{Cl} ($l = 1.58$; $m = 0.82$) are very similar to those for octyl fluoroformate and several chloroformate esters, which are believed to solvolyze by an addition−elimination (association−dissociation) mechanism, with the addition step being rate determining.

The k_{Cl}/k_F ratios, readily determined by using data available for the solvolysis of benzoyl chloride, are all appreciably larger than unity, in contrast to values of close to unity for the octyl haloformates. Several very large values result from the solvolysis involving a solvent for which the k_{Cl} value is measuring a superimposed ionization pathway. However, appreciable values (>38) are observed when both halides are believed to operate by a bimolecular pathway. As water is added to the organic component of binary mixtures with ethanol, methanol, and acetone, the values fall from the 350−700 range to a value of about 40 and then steadily rise again as the region is entered where ionization is known to be dominant for benzoyl chloride solvolysis. With *p*-nitrobenzoyl halide solvolyses, it is known that the addition−elimination pathway will be dominant for both halides, except in 97% HFIP, and the k_{Cl}/k_F value continues to fall, reaching a value of 1.2 in 100% H_2O. It is suggested that for the bimolecular pathway the major influence of varying the halogen is a more pronounced ground-state stabilization for the fluoride, rather than increased return from a tetrahedral intermediate. For haloformates, the ground-state stabilization is largely provided by the oxygen attached to the carbonyl carbon.

Using literature values, it is possible to consider k_{Br}/k_{Cl} ratios as well. These show only modest variation with either solvent composition or an introduction of *p*-methoxy, *p*-methyl, or *p*-chloro substituents, with an overall range of values of 20−135. However, high reactivity at 25 °C and low solubility at reduced temperatures prevented the study of the solvolysis of the bromides in aqueous−organic solvents with more than 30% water content.

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The acid catalysis frequently observed for solvolyses of acyl fluorides does not necessarily arise because the conversion to a better leaving group aids C−F bond fission. It could involve a ground-state effect, with change from Coulombic stabilization to Coulombic destabilization leading to a considerably higher energy substrate and a lower energy barrier to reaction.

Experimental Section

Commercially available benzoyl fluoride (purity 99.5%) was used as received. The determinations of specific rates of solvolysis were as previously described.[21,27] The multiple regression analyses were carried out with the ABSTAT statistical package (Anderson-Bell, Arvada, Colorado).

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