

## Application of the Extended Grunwald-Winstein Equation to Solvolyses of *n*-Propyl Fluoroformate and a Consideration of Leaving Group Effects

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Reactions of *n*-propyl fluoroformate in a variety of pure and binary solvents have been studied at 40.0 °C. The extended (two-term) Grunwald-Winstein equation has been applied to the specific rates of solvolysis of *n*-propyl fluoroformate. The sensitivities ( $l = 1.80 \pm 0.17$  and  $m = 0.96 \pm 0.10$ ) to changes in solvent nucleophilicity and solvent ionizing power and the  $k_F/k_{Cl}$  values are similar to those for solvolyses of *n*-octyl fluoroformate over the full range of solvents, suggesting that the addition step of an addition-elimination mechanism is rate-determining. These observations are also compared with those previously reported for the corresponding chloroformate and fluoroformate esters.

**Key Words:** *n*-Propyl fluoroformate. Addition-elimination, Grunwald-Winstein equation. Leaving group effect

### Introduction

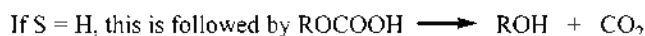
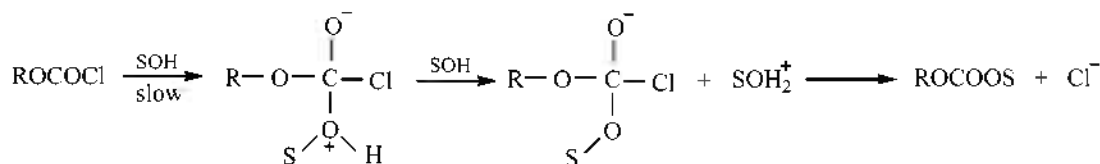
Recently, the solvolyses of *n*-propyl chloroformate<sup>1</sup> in a variety of pure and binary solvents were found to involve the reaction following the addition-elimination pathway in the majority of the solvents but an ionization pathway in the solvents of highest ionizing power and lowest nucleophilicity. For solvolyses of 1-adamantyl chloroformate,<sup>2</sup> the ionization pathway was dominant in all solvents and only in 100% ethanol was a trace of the mixed carbonate observed. However, replacement of chlorine by fluorine (1-adamantyl fluoroformate<sup>3</sup>) led to behavior very similar to that previously observed for the solvolyses of *n*-propyl chloroformate, which have been shown to solvolyze with the addition step of an addition-elimination pathway in all solvents but the most ionizing and weakly nucleophilic solvents. For the bimolecular hydrolyses of a pair of fluoroformate and chloroformate esters,<sup>4</sup> the addition step was believed to be

rate determining, largely on the basis of the similar rates for the two halogenoformate esters, despite the stronger carbon-fluorine bond. Particularly, the comparison of leaving group effects ( $k_F/k_{Cl}$  ratios) on the rates of solvolysis of chloroformate and fluoroformate esters has provided useful information about the reaction mechanism. Similar ratios of  $k_F/k_{Cl}$  specific rates have been observed previously for the solvolyses of other haloformate esters.<sup>5-8</sup> For example,  $k_F/k_{Cl}$  ratios of 1.09 to 7.16 for 70% aqueous acetone at 30.1 °C have been reported.<sup>4</sup> For solvolyses, the two proposed nucleophilic substitution mechanisms can be expressed as an addition-elimination mechanism (Scheme 1) and as an ionization mechanism (Scheme 2).

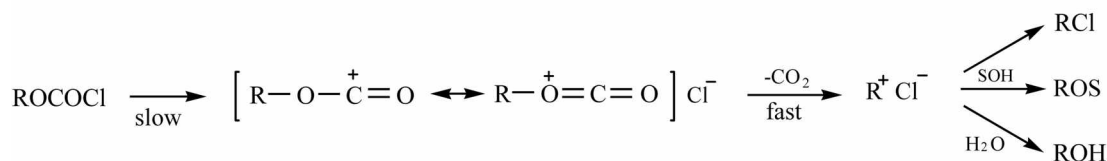
The extended Grunwald-Winstein (equation (1)) can be applied as a powerful mechanistic tool.<sup>5,10</sup>

$$\log(k/k_0) = lN_T - mY_N + c \quad (1)$$

In equation (1),  $k$  and  $k_0$  are the specific rates of solvolysis



Scheme 1



Scheme 2

of a substrate RX in a given solvent and in the standard solvent (80% ethanol), respectively;  $l$  is the sensitivity toward changes in solvent nucleophilicity  $N_T$ ;  $m$  is the sensitivity toward changes in solvent ionizing power  $Y_{Cl}$ ;  $c$  is a constant (residual) term. Scales of solvent nucleophilicity and of solvent ionizing power are available and, by measuring  $k$  and  $k_0$ , one can carry out a mathematical analysis to obtain the  $l$  and  $m$  values. For an ionization reaction without nucleophilic assistance,  $l$  will be zero and  $m$  close to unity. Accordingly, determination of the  $l$  and  $m$ -values will be a valuable source of information concerning the structure of the transition state for these solvolyses.

In this work, we determine the overall specific rates for solvolyses of *n*-propyl fluoroformate in a variety of pure and binary solvents. The solvolyses of several chloroformate esters divided, in the usually studied solvents, into two almost equally sized groups, with either ionization or addition-elimination as the rate-determining step.<sup>14</sup> Mechanistic conclusions are then drawn from a consideration of the analyses using the extended Grunwald-Winstein equation, including a comparison with the  $l$  and  $m$  values determined from a combination of published and new kinetic data for solvolyses of *n*-propyl fluoroformate. In addition to an extended Grunwald-Winstein equation of the specific rates, these analyses are combined with a consideration of leaving group effects to arrive at a reasonable mechanism.

### Materials and Methods

**Materials.** The *n*-propyl chloroformate (Aldrich) was purified by fractional distillation at reduced pressure. The *n*-propyl chloroformate (5.0 g, 0.041 mol) was syringed into a three-neck flask (250 mL) containing dried KF (3.45 g, 0.059 mol) and 18-crown-6 (0.42 g, 0.0016 mol) and fitted with a Teflon stirring bar, a condenser topped by an N<sub>2</sub> gas inlet, a septum cap, and a ground glass stopper, as described earlier.<sup>15</sup> The mixture then was stirred efficiently at room temperature until FT-IR (Bio-Red FTS 6000) analysis of an aliquot indicated that no chloroformate remained (C=O stretch at 1752 cm<sup>-1</sup>; fluoroformate C=O stretch at 1830 cm<sup>-1</sup>). After a reaction time of 45 hours, the *n*-propyl fluoroformate was isolated directly from the reaction apparatus by simple distillation at a reaction temperature of 91–93 °C. The solvents were purified as previously described.<sup>8</sup>

**Methods.** The kinetic runs were carried out as previously described.<sup>8,16</sup> The rates of production of hydrofluoric acid were followed for solvolyses in methanol, ethanol, aqueous-organic mixtures, and TFE-ethanol mixtures. Portions were removed at appropriate time intervals and partitioned between 20 mL of pentane and 10 mL of degassed distilled water. The acid previously developed was then titrated against a standardized solution of NaOH in water (*ca.* 5.00 × 10<sup>-3</sup> M) to a methylene blue-methyl red endpoint.<sup>16</sup> Runs in 2,2,2-trifluoroethanol (TFE)-H<sub>2</sub>O solvents and in TFE-EtOH solvents involved removal of 2 mL portions from 25 mL, and runs in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)-H<sub>2</sub>O solvents involved removal of 1 mL portions from 10

mL, and runs in other solvents involved removal of 5 mL portions from 50 mL. The substrate concentration was about 5.00 × 10<sup>-3</sup> M. Experimental infinity titers were obtained after at least ten half-lives and the determinations of the first-order rate coefficients (specific rates) of solvolysis were calculated from the equation (2). In equation (2),  $V_0$  is the titer at time zero (when first portion is removed),  $V_t$  is the titer at time ( $t$ ) of removal of a subsequent portion, and  $V_\infty$  is the titer for a portion removed after at least ten half-lives. The  $l$  and  $m$  values were calculated using commercially available computer programs for multiple regression analyses.

$$k = \frac{1}{t} \ln \frac{(V_\infty - V_0)}{(V_\infty - V_t)} \quad (2)$$

### Results and Discussion

The specific rates of solvolysis of *n*-propyl fluoroformate were determined in 20 solvents at 40.0 °C. The solvents consisted of ethanol, methanol, binary mixtures of water with ethanol (EtOH), methanol (MeOH), acetone (Me<sub>2</sub>CO), TFE, or HFIP, and four binary mixtures of TFE and ethanol (T-E). The specific rates of solvolysis are presented in Table 1, together with  $N_T$  and  $Y_{Cl}$  values. Specific rates of solvolysis of *n*-propyl chloroformate were determined in six solvents at the same temperature. These values are reported in Table 2, together with the  $k_F/k_{Cl}$  ratios.

An analysis of the 19 specific rates of Table 1 leads, in

**Table 1.** Specific rates of solvolysis of *n*-propyl fluoroformate in a variety of pure and mixed solvents at 40.0 °C and the  $N_T$  and  $Y_{Cl}$  values for the solvents

Solvent <sup>a</sup>	10 <sup>4</sup> $k$ (s <sup>-1</sup> )	$N_T$ <sup>b</sup>	$Y_{Cl}$ <sup>c</sup>
100% MeOH	2.19 ± 0.04 <sup>d</sup>	0.17	-1.17
90% MeOH	18.8 ± 0.4	-0.01	-0.18
80% MeOH	37.4 ± 2.0	-0.06	0.67
100% EtOH	0.437 ± 0.020	0.37	-2.52
90% EtOH	6.79 ± 0.15	0.16	-0.94
80% EtOH	14.0 ± 0.5	0.00	0.00
70% EtOH	23.7 ± 0.5	-0.20	0.78
80% Me <sub>2</sub> CO	0.785 ± 0.047	-0.37	-0.83
70% Me <sub>2</sub> CO	2.58 ± 0.16	-0.42	0.17
90% TFE	0.123 ± 0.021	-2.55	2.85
70% TFE	2.20 ± 0.06	-1.98	2.96
50% TFE	10.8 ± 0.7	-1.73	3.16
80T-20E <sup>e</sup>	0.144 ± 0.024	-1.76	1.89
60T-40E <sup>e</sup>	0.321 ± 0.055	-0.94	0.63
40T-60E <sup>e</sup>	0.532 ± 0.024	-0.34	-0.48
20T-80E <sup>e</sup>	0.926 ± 0.051	0.08	-1.42
90% HFIP	0.0213 ± 0.0010	-3.84	4.31
70% HFIP	0.761 ± 0.032	-2.94	3.83
50% HFIP	7.00 ± 0.36	-2.49	3.80

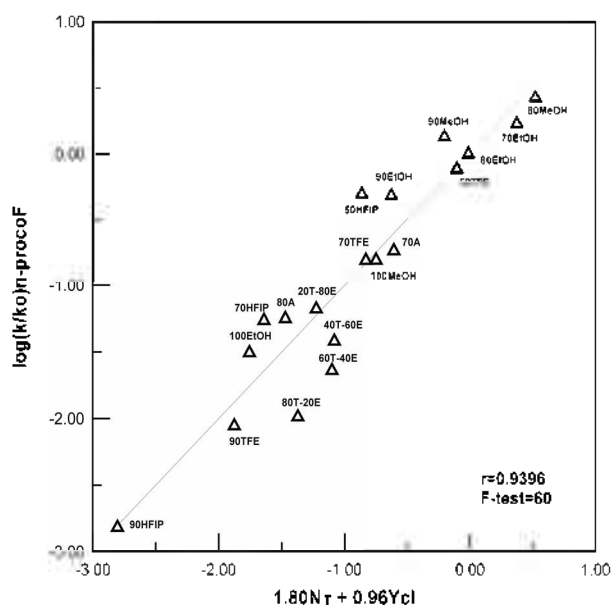
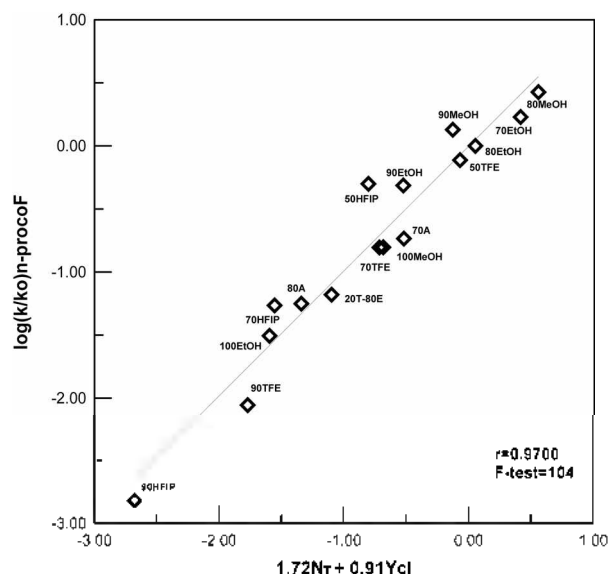
<sup>a</sup>Volume/volume basis at 25.0 °C, except for TFE-H<sub>2</sub>O, HFIP-H<sub>2</sub>O mixtures, which are on a weight/weight basis. <sup>b</sup>Values from refs. 10, 11. <sup>c</sup>Values from refs. 12, 13. <sup>d</sup>Value in CH<sub>3</sub>OD of (0.659 ± 0.020) 10<sup>4</sup> sec<sup>-1</sup>, and solvent deuterium isotope effect ( $k_{MeOH}/k_{MeOD}$ ) of 3.32. <sup>e</sup>T-E are 2,2,2-trifluoroethanol-ethanol mixtures.

**Table 2.** Specific rates of the solvolyses of *n*-propyl chloroformate in a variety of pure and mixed solvents at 40.0 °C and  $k_F/k_{Cl}$  specific rate ratios

Solvent <sup>a</sup>	$10^5 k_{F/OCOCl}$ , s <sup>-1</sup>	$k_{F/OCOCl}/k_{Cl/OCOCl}$ <sup>b</sup>
100% EtOH	$7.73 \pm 0.02$	0.57
80% EtOH	$24.9 \pm 0.3$	5.62
100% MeOH	$29.4 \pm 0.6$	0.75
70% Me <sub>2</sub> CO	$6.09 \pm 0.01$	4.24
70% TFE	$2.85 \pm 0.02$	7.72
70% HFIP	$2.77 \pm 0.03$	2.75

<sup>a</sup>Volume/volume basis at 25.0 °C, except for TFE-H<sub>2</sub>O, HFIP-H<sub>2</sub>O mixtures, which are on a weight/weight basis. <sup>b</sup>Specific rates of solvolysis of *n*-propyl fluoroformate are from Table 1.

terms of the simple Grunwald-Winstein equation [equation (1) without the  $fN_T$  term], to a very poor correlation with value 0.208 for the correlation coefficient. An analysis of the data obtained by applying the modified form of the Grunwald-Winstein equation [eqn. (1)] to the specific rates of solvolysis of *n*-propyl fluoroformate leads to an acceptable linear correlation with values of  $1.80 \pm 0.17$  for  $l$ ,  $0.96 \pm 0.10$  for  $m$ ,  $-0.01 \pm 0.1$  for  $c$ . The correlation coefficient ( $r$ ) is still rather low at 0.940 and the F-test value is 60. Inspection of the plot corresponding to this correlation (Figure 1) shows that three binary mixtures of TFE and ethanol (80T-20E, 60T-40E, and 40T-60E mixtures) lie below the best fit line. In earlier correlations of other haloformate esters, it was found that the data points for TFE-ethanol solvent systems usually lie below the correlation line.<sup>17-19</sup> This phenomenon was very recently discussed and it will not be considered again in this paper.<sup>20</sup> When these data points are omitted from the correlation, the  $l$  and  $m$  values are only slightly reduced but considerably improved values for the correlation coefficient ( $r = 0.970$ ) and for the F-test value (F-test = 104) are observed (Figure 2 and Table

**Figure 1.** Plot of  $\log(k/k_0)$  for solvolyses of *n*-propyl fluoroformate in pure and binary solvents at 40.0 °C against  $(1.80N_T + 0.96Y_{Cl})$ .**Figure 2.** Plot of  $\log(k/k_0)$  for solvolyses of *n*-propyl fluoroformate in pure and binary solvents at 40.0 °C against  $(1.72N_T + 0.91Y_{Cl})$ , with omission of the three data points for 80T-20E, 60T-40E, and 40T-60E.

3). The correlation is presented in Figure 1 and included in Table 3, together with the corresponding parameters obtained for earlier studied substrates. The  $l$  and  $m$  values for the solvolysis of *n*-propyl fluoroformate, respectively, were similar to values previously reported for bimolecular solvolyses of other chloroformate and fluoroformate esters, believed to solvolyse by an addition-elimination mechanism, with the addition being rate-determining. An LFER plot of  $\log(k/k_0)$  for *n*-propyl fluoroformate against  $\log(k/k_0)$  for *n*-octyl fluoroformate shows a good linear correlation ( $r = 0.985$ ) in pure and mixed solvents, giving a strong evidence for a similar solvolysis mechanism.

The specific rate ratios ( $k_F/k_{Cl}$ ) of solvolysis of *n*-propyl fluoroformate and chloroformate show with values ranging from 0.57 in ethanol to 7.72 in 70%TFE (Table 2). A recent report concerning the solvolyses of *n*-octyl fluoroformate and chloroformate found the  $k_F/k_{Cl}$  ratio to be somewhat below unity in ethanol and methanol and to be slightly greater than unity for solvolyses in mixtures of water with ethanol, acetone, or TFE.<sup>7</sup> As mentioned above, for binary solvents, the fluoroformate is somewhat faster, despite the stronger carbon-fluorine bond. Since the carbon-fluorine bond is much stronger than the carbon-chlorine bond, if the carbon-halogen bond is broken in the rate-determining,  $k_F/k_{Cl}$  ratios would be expected to exhibit a marked leaving group effect,  $k_F \ll k_{Cl}$ . However, bimolecular pathway through a tetrahedral intermediate formed by rate-determining addition of the solvent at the carbonyl carbon would be characterized by  $k_F \geq k_{Cl}$ .

The consideration of  $k_F/k_{Cl}$  ratios in nucleophilic substitution reactions has long been recognized as a useful tool in studying the reaction mechanism.<sup>21</sup> This is especially so when the attack is at an acyl carbon. When the carbon-halogen bond is broken in a nucleophilic displacement reac-

**Table 3.** Correlation of the specific rates of solvolysis of *n*-propyl fluoroformate and a comparison with corresponding values for the solvolyses of other chloroformate and fluoroformate esters using the extended Grunwald-Winstein<sup>a</sup>

Substrate	Mech. <sup>b</sup>	<i>n</i> <sup>c</sup>	<i>l</i> <sup>d</sup>	<i>m</i> <sup>d</sup>	<i>c</i> <sup>d</sup>	<i>R</i> <sup>e</sup>	<i>l/m</i>
PhOCOC1	A-E	21 <sup>f</sup>	1.68 ± 0.10	0.57 ± 0.06	0.12 ± 0.41	0.973	2.95
<i>n</i> -PrOCOC1	A-E	22 <sup>g</sup>	1.57 ± 0.12	0.56 ± 0.06	0.15 ± 0.08	0.947	2.79
<i>n</i> -PrOCOC1	I	6 <sup>h</sup>	0.40 ± 0.12	0.64 ± 0.13	-2.45 ± 0.47	0.942	0.63
<i>n</i> -PrOCOF	A-E	19 <sup>b</sup>	1.80 ± 0.17	0.96 ± 0.10	-0.01 ± 0.11	0.940	1.88
<i>n</i> -PrOCOF	A-E	16 <sup>b</sup>	1.72 ± 0.12	0.91 ± 0.08	0.05 ± 0.08	0.970	1.89
<i>i</i> -PrOCOC1	I	20 <sup>i</sup>	0.28 ± 0.05	0.52 ± 0.03	-0.12 ± 0.05	0.979	0.54
<i>i</i> -PrOCOF	A-E	20 <sup>j</sup>	1.59 ± 0.16	0.80 ± 0.06	0.06 ± 0.08	0.957	1.99
OctOCOF	A-E	23 <sup>k</sup>	1.80 ± 0.13	0.79 ± 0.06	0.13 ± 0.34	0.959	2.28
C <sub>6</sub> H <sub>5</sub> COF	A-E	41 <sup>l</sup>	1.58 ± 0.09	0.82 ± 0.05	-0.09 ± 0.10	0.953	1.93
1-AdOCOC1	I	15 <sup>m</sup>	~0	0.47 ± 0.03	0.03 ± 0.05	0.985	~0

<sup>a</sup>Using equation 1. <sup>b</sup>Addition-elimination (A-E) and ionization (I). <sup>c</sup>Number of solvent systems included in the correlation. <sup>d</sup>Using equation 1, with standard errors for *l* and *m* values and with the standard errors of the estimate accompanying the *c* value. <sup>e</sup>Correlation coefficient. <sup>f</sup>Values from ref. 19. <sup>g</sup>Values from ref. 1 and the solvent systems divided into 100% TFE, 97% TFE, and all HFIP-H<sub>2</sub>O mixtures (*n* = 6). <sup>h</sup>This study and with omission of the three TFE-EtOH solvents (*n* = 17). <sup>i</sup>Values from ref. 28. <sup>j</sup>Values from ref. 25. <sup>k</sup>Values from ref. 7. <sup>l</sup>Values from ref. 24. <sup>m</sup>Values from ref. 2.

tion, the specific rates of fluoro-derivative react appreciably slower than that for chloro-derivative. For some examples of S<sub>N</sub>1 reaction, a value as low as the  $k_F/k_{Cl}$  rate ratio, 10<sup>-7</sup> was observed in 4-(*N,N*-dimethylamino)benzoyl halide solvolyses<sup>22</sup> and a low value of 1.3 × 10<sup>-4</sup> was also observed for acetyl halide solvolyses in 75% acetone.<sup>21</sup> These values reflect an appreciable ground-state stabilization for the fluoride<sup>23</sup> and the need to break a strong carbon-fluorine bond in the rate determining step. In contrast, if the addition step is rate-determining, values of close to unity (and frequently above it), reflecting a large electron deficiency at the carbonyl carbon of a haloformate incorporating fluorine,<sup>24</sup> are frequently observed. For a meaningful comparison of the specific rates ( $k_F/k_{Cl}$ ) of solvolysis of *n*-propyl fluoroformate and chloroformate at 40.0 °C in Table 2, it is important that the comparison is for the same reaction pathway. The ratios vary from a low of 0.57 in ethanol (0.60 for *n*-octyl haloformate in ethanol<sup>7</sup>) to a high of 7.72 in 70% TFE (10.2 for *n*-octyl haloformate in 80% TFE<sup>7</sup>). The  $k_F/k_{Cl}$  specific rate ratios for a variety of pure and mixed solvents (Table 2) are similar to the values for reaction of *n*-octyl haloformate which has been shown to solvolyze by the bimolecular addition-elimination mechanism, proceeding through a tetrahedral intermediate.<sup>7</sup>

The values of Table 3 divide into two principal mechanisms, *i.e.*, the so-called bimolecular mechanism postulated to represent addition-elimination pathway (Scheme 1) and unimolecular mechanism believed to represent ionization pathway (Scheme 2). For *n*-propyl fluoroformate, the value for the ratio (*l/m*) of 1.89 is very similar to those previously observed for the solvolyses of *i*-propyl fluoroformate,<sup>25</sup> *n*-octyl fluoroformate<sup>7</sup> and benzoyl fluoride,<sup>24</sup> which have been shown to solvolyze with the addition step of an addition-elimination pathway being rate determining. The higher *m*-values for the solvolyses of fluoroformates, relative to chloroformates, may reflect the need for increased solvation of the developing negative charge on the carbonyl oxygen in the presence of the more electronegative fluorine attached at the carbonyl carbon.

For methanolysis of *n*-propyl fluoroformate, the kinetic solvent isotope effect (KSIE) value using methanol-*d* was presented in footnote to Table 1. The  $k_{MeOH}/k_{MeOD}$  value of 3.32 for *n*-propyl fluoroformate is higher than for the methanolysis of *n*-propyl chloroformate ( $k_{MeOH}/k_{MeOD}$  = 2.17)<sup>1</sup> or for the ethanolysis of a series of *para*-substituted phenyl chloroformates, where values in the range of 2.1-2.4 were obtained.<sup>26,27</sup> The higher value gives further support for the proposal that bond formation is more advanced at the transition state for addition to fluoroformates than for chloroformates.

## Conclusions

The specific rates of solvolyses of *n*-propyl fluoroformate give a satisfactory extended Grunwald-Winstein correlation (equation 1) over the full range of solvents. The *l* and *m* parameters obtained from the extended Grunwald-Winstein treatment of the specific rates of solvolyses of *n*-propyl fluoroformate are very similar to those previously obtained for the several fluoroformate and chloroformate esters (Table 3).

The  $k_F/k_{Cl}$  values obtained in a comparison with the corresponding solvolysis of *n*-propyl chloroformate are similar to those for solvolyses of *i*-propyl haloformate,<sup>25</sup> *n*-octyl haloformate<sup>7</sup> and benzoyl halide,<sup>24</sup> consistent with a bimolecular addition-elimination mechanism, proceeding through a tetrahedral intermediate. Favoring an explanation in terms of alkyl variation is the observation that the  $k_F/k_{Cl}$  ratio for solvolyses of haloformate esters in 70% acetone at 30.1 °C decreases from methyl (7.16),<sup>4</sup> ethyl (5.46)<sup>4</sup> or *n*-propyl (the  $k_F/k_{Cl}$  ratio of *n*-propyl group in 70% acetone at 40.0 °C is 4.24 at Table 2) to isopropyl (1.09)<sup>4</sup>, suggesting that a value of less than unity would be observed upon incorporation of a bulky secondary alky group. This trend could possibly be governed by increasing steric effects.

In the present study, unlike the reactions in hydroxylic solvents of *n*-propyl chloroformate, where both the bimolecular pathway (Scheme 1) and the unimolecular pathway

(Scheme 2) were observed, the solvolyses of *n*-propyl fluoroformate all follow the pathway involving rate-determining bimolecular attack by solvent at acyl carbon.

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