

# Correlation of the Rate of Solvolysis of Neopentyl Fluoroformate and a Consideration of Alkyl Haloformates in Solvolytic Reactions

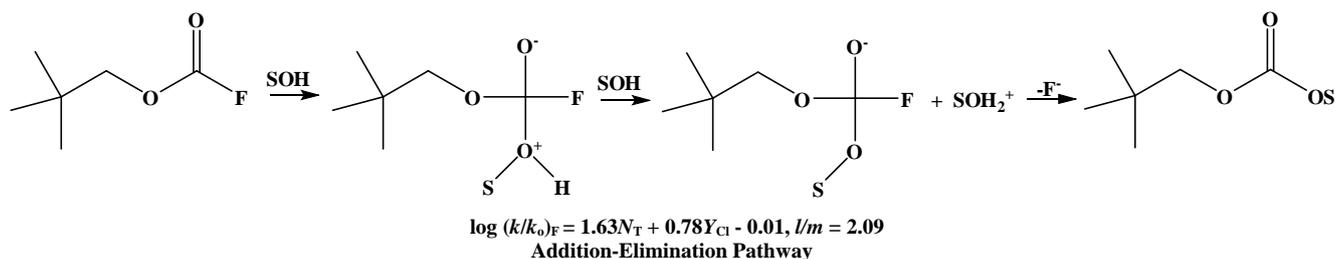
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## Graphic Abstract



**Abstract** -The specific rates of solvolysis of neopentyl fluoroformate (NeopOCOF, 1) have been measured at 45.0 °C in pure and binary solvent mixtures. These results correlated well with the extended Grunwald-Winstein equation in all of the solvents except the four TFE-ethanol binary solvents. Leaving group effects ( $k_F/k_{Cl}$  values) and sensitivity ( $l$  and  $m$  values) to changes in solvent nucleophilicity and solvent ionizing power are appreciably similar to those observed previously for the solvolyses of primary and secondary alkyl haloformates. This is consistent with the addition-elimination pathway as rate-determining. The kinetic solvent isotope effects (KSIEs,  $k_{MeOH}/k_{MeOD}$ ) and activation parameters for the solvolyses of 1 were also determined. The results are compared with those reported earlier for neopentyl chloroformate (NeopOCOCl, 2) and other alkyl haloformate esters.

**Keywords**- Neopentyl Fluoroformate; Grunwald-Winstein Equation; Leaving Group Effect; Solvolytic Reaction; Addition-Elimination Pathway

## I. INTRODUCTION

Correlation analysis with the original Grunwald-Winstein (G-W) Equation (1) and the extended G-W Equation (2) has long been employed as a diagnostic tool for studying solvent effects on solvolytic reactions<sup>[1,2]</sup>.

$$\log(k/k_o) = mY_{Cl} \quad (1)$$

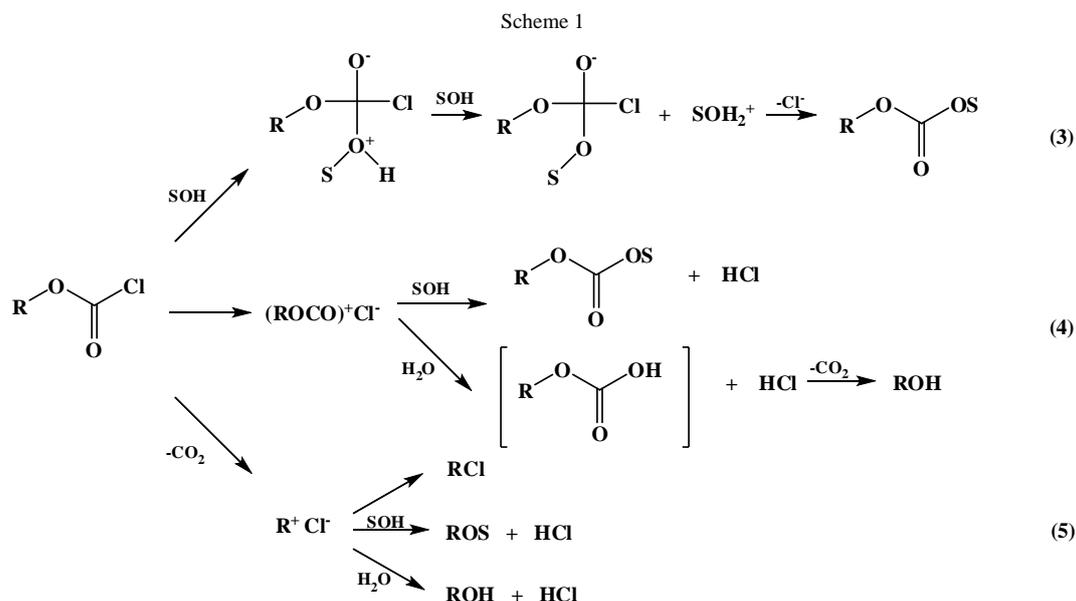
$$\log(k/k_o) = lN_T + mY_{Cl} \quad (2)$$

In Equations (1) and (2),  $k$  and  $k_o$  represent the specific rates of solvolysis in a given solvent and in the standard solvent (80% ethanol), respectively;  $m$  is the sensitivity towards changes in  $Y_{Cl}$ <sup>[3]</sup>, a scale of solvent ionizing power based on the specific rates of solvolysis of 1-adamantyl chloride; and  $l$  is the sensitivity towards changes in  $N_T$ <sup>[4]</sup>, a scale of solvent nucleophilicity based on the specific rates of solvolysis of the *S*-methylidibenzothiophenium ion, which is influenced little by changes in solvent ionizing power.  $N_T$  values have been recognized as standards for considerations of solvent nucleophilicity. The magnitudes of the  $l$  and  $m$  values can give important indications regarding the mechanism of solvolysis.

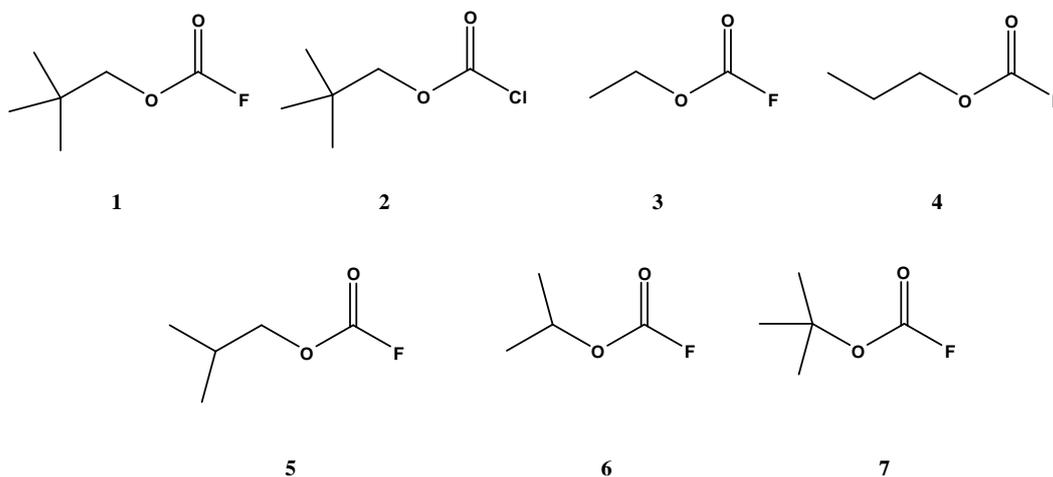
We previously reported that the solvolyses of 2 in solvents of low ionization power and/or high nucleophilicity follow an addition-elimination mechanism [Equation (3)], as found using either the original [Equation (1)] or extended [Equation (2)] G-W equations<sup>[5]</sup>. Only in solvents of very low nucleophilicity and very high ionizing power (e.g., the solvolysis of 2 in aqueous fluoroalcohol solvents) can an ionization pathway [Equation (5)] be detected. The kinetics of the solvolysis of alkyl haloformate esters has been extensively studied for many years. However, the kinetics and mechanism of alkyl fluoroformates have been studied less extensively than alkyl chloroformates. A recently published study<sup>[5]</sup> of the multiple pathways in the solvolysis of 2 is extended to 1.

The overall solvolyses of primary, secondary and tertiary chloroformates in hydroxylic solvents can be expressed according

to Scheme 1. The pathways involve bimolecular substitution at the acyl carbon, as shown in Equation (3), and a rate-determining unimolecular reaction with accompanying loss of carbon dioxide or carboxylium ion, as shown in Equations (4) and (5)<sup>[6]</sup>.



We have investigated the specific rates for solvolyses of 1 in a wide range of solvent types. Mechanistic conclusions were then drawn from analyses using the G-W equation, including a comparison with the *l* and *m* values previously determined from kinetic studies of other haloformate esters. We also report solvolysis studies at three different temperatures in four organic solvents to determine the values of enthalpy and entropy of activation and the kinetic solvent isotope effect for methanolysis. By comparing with the values for the solvolyses of 2, leaving-group effects were considered to arrive at a reasonable mechanism. These observations are also compared with those reported earlier for the corresponding alkyl haloformate esters, ethyl- (EtOCOF, 3)<sup>[7(a)]</sup>, *n*-propyl- (*n*-PrOCOF, 4)<sup>[7(b)]</sup>, *i*-butyl- (*i*-BuOCOF, 5)<sup>[7(c)]</sup>, *i*-propyl- (*i*-PrOCOF, 6)<sup>[7(d)]</sup>, and *t*-butyl (*t*-BuOCOF, 7)<sup>[7(e)]</sup> fluoroformates.



## II. RESULTS AND DISCUSSION

The specific rates of the solvolysis of 1 were measured in 18 solvents at 45.0°C. The solvents consisted of methanol, ethanol, binary mixtures of water with methanol (MeOH), ethanol (EtOH), 2,2,2-trifluoroethanol (TFE), acetone plus four binary mixtures of TFE and EtOH. The specific rates of solvolysis of 1 are reported in Table 1 together with the  $N_T$  and  $Y_{Cl}$ , and the KSIEs values in methanol-*d* (footnote to Table 1). Table 1 also contains the relative ratios of the specific rate of solvolysis of 1 to that of 2 for each solvent. The specific rates of solvolysis of 1 and 2 were determined at three different temperatures in MeOH, EtOH, 80% EtOH, and 70% TFE, and these values and the calculated enthalpies and entropies of activation are reported in Table 2.

TABLE I SPECIFIC RATES OF SOLVOLYSIS OF 1<sup>A</sup> IN PURE AND MIXED SOLVENTS AT 45.0 °C ALONG WITH THE APPROPRIATE SOLVENT NUCLEOPHILICITY ( $N_T$ ), SOLVENT IONIZING POWER ( $Y_{Cl}$ ), AND  $k_F/k_{Cl}$  VALUES

Solvent (%) <sup>b</sup>	10 <sup>4</sup> $k$ , s <sup>-1</sup>	$N_T$ <sup>c</sup>	$Y_{Cl}$ <sup>d</sup>	$k_F/k_{Cl}$ <sup>e</sup>
100EtOH	0.548±0.005	0.37	-2.52	0.34
90EtOH	8.36±0.04	0.16	-0.94	3.02
80EtOH	16.5±0.40	0.00	0.00	4.81
70EtOH	25.6±0.30	-0.20	0.78	-
100MeOH <sup>f</sup>	2.94±0.03	0.17	-1.17	0.61
90MeOH	24.3±0.19	-0.01	-0.18	3.13
80MeOH	49.4±0.34	-0.06	0.67	5.41
90Acetone	0.115±0.003	-0.35	-2.22	1.43
80Acetone	0.876±0.003	-0.37	-0.83	2.93
70Acetone	2.74±0.044	-0.42	0.17	3.50
60Acetone	6.76±0.028	-0.52	0.95	5.77
90TFE <sup>g</sup>	0.147±0.004	-2.55	2.85	1.29
70TFE <sup>g</sup>	2.56±0.016	-1.98	2.96	6.28
50TFE <sup>g</sup>	8.49±0.054	-1.73	3.16	10.8
80T-20E <sup>h</sup>	0.0556±0.0008	-1.76	1.89	1.22
60T-40E <sup>h</sup>	3.38±0.076	-0.94	0.63	-
40T-60E <sup>h</sup>	6.40±0.05	-0.34	-0.48	1.44
20T-80E <sup>h</sup>	6.92±0.04	0.08	-1.42	0.61

<sup>a</sup> Substrate concentration of  $5.86 \times 10^{-3}$  mol dm<sup>-3</sup>. <sup>b</sup> Unless otherwise indicated, on a volume/volume basis at 25.0 °C, with the other component as water. <sup>c</sup> Values from ref. 4. <sup>d</sup> Values from ref. 3 <sup>e</sup> Values relative to those for the corresponding solvolysis of neopentyl chloroformate (values from ref. 5.). <sup>f</sup> Value in 100% MeOD of  $(0.863 \pm 0.010) \times 10^{-4}$  s<sup>-1</sup>, leading to a  $k_{MeOH}/k_{MeOD}$  value of  $3.40 \pm 0.02$  and specific rates of solvolysis of neopentyl chloroformate (2) in 100% MeOH and MeOD at 45.0 °C are  $(4.59 \pm 0.16)_{MeOH} \times 10^{-4}$  s<sup>-1</sup> and  $(2.07 \pm 0.01)_{MeOD} \times 10^{-4}$  s<sup>-1</sup>, respectively. The  $k_{MeOH}/k_{MeOD}$  value of solvolysis of neopentyl chloroformate (2) is 1.77. <sup>g</sup> Solvents prepared on weight/weight basis. <sup>h</sup> T-E represents 2,2,2-trifluoroethanol-ethanol mixtures

TABLE II SPECIFIC RATES FOR SOLVOLYSIS OF NEOPENTYL FLUOROFORMATE (NeopOCOF, 1)<sup>A</sup> AND NEOPENTYL CHLOROFORMATE (NeopOCOCl, 2)<sup>B</sup> AT VARIOUS TEMPERATURES AND ENTHALPIES ( $\Delta H^\ddagger$ , kcal mol<sup>-1</sup>) AND ENTROPIES ( $\Delta S^\ddagger$ , cal mol<sup>-1</sup> K<sup>-1</sup>) OF ACTIVATION AT 45.0 °C

Solvent (%) <sup>c</sup>	Temp (°C)	NeopOCOF			Temp (°C)	NeopOCOCl		
		10 <sup>4</sup> $k_F$ , s <sup>-1</sup>	$\Delta H^\ddagger_{318}$ <sup>d</sup>	$-\Delta S^\ddagger_{318}$ <sup>d</sup>		10 <sup>4</sup> $k_{Cl}$ , s <sup>-1</sup>	$\Delta H^\ddagger_{318}$ <sup>d</sup>	$-\Delta S^\ddagger_{318}$ <sup>d</sup>
100MeOH	25.0	0.932±0.007	10.4±0.1	44.6±0.4	45.0	4.79±0.03 <sup>f</sup>	15.1±0.4	38.6±1.4
	40.0	2.25±0.06			50.0	6.74±0.06		
	45.0	2.69±0.09 <sup>e</sup>			55.0	9.60±0.07		
	50.0	3.94±0.02			60.0	13.3±0.2		
100EtOH	25.0	0.155±0.003	11.4±0.1	42.3±0.4	45.0	1.46±0.03 <sup>g</sup>	12.9±0.8	35.6±2.4
	40.0	0.405±0.004			50.0	1.84±0.02		
	45.0	0.548±0.006 <sup>e</sup>			55.0	2.64±0.05		
	50.0	0.752±0.007			65.0	5.06±0.03		
80EtOH	25.0	6.16±0.03	8.8±0.2	45.1±0.6	45.0	3.65±0.04 <sup>h</sup>	13.3±0.2	38.8±0.5
	40.0	13.3±0.3			55.0	7.23±0.04		
	45.0	16.5±0.3 <sup>e</sup>			60.0	10.1±0.1		
	50.0	21.5±0.2			65.0	13.2±0.1		
70TFE	25.0	0.660±0.020	12.0±0.1	37.4±0.3	45.0	0.407±0.002 <sup>f</sup>	20.0±0.5	15.8±1.6
	40.0	1.83±0.02			60.0	1.66±0.02		
	45.0	2.56±0.02 <sup>e</sup>			65.0	0.274±0.010		
	50.0	3.41±0.06			70.0	4.46±0.04		

<sup>a, c, e</sup> See footnotes to Table 1. <sup>b</sup> Substrate concentration of  $5.33 \times 10^{-3}$  mol dm<sup>-3</sup>. <sup>d</sup> With associated standard error. <sup>f</sup> From ref. 5. <sup>g</sup> Value of 1.63 at 45.0 °C (ref. 5). <sup>h</sup> Value of 3.43 at 45.0 °C (ref. 5).

It is of interest to compare the specific rates for 1 with those for the previously studied alkyl fluoroformates<sup>[7]</sup>. As is the nature of nucleophilic acyl substitution reactions, the rate of addition to the carbonyl carbon decreased as the steric demands of alkyl group (*i.e.*, branching at the  $\alpha$ -carbon) increase. The rate of the reaction was enhanced as the electron withdrawing ability of the alkoxy group increased the positive charge on the carbonyl carbon (electronic effects)<sup>[8]</sup>. Table 3 shows the order of the specific rate for the solvolyses of 1 in relation to those previously studied for primary, secondary and tertiary alkyl fluoroformates as  $k_{Me} > k_3 \approx k_4 \approx k_5 \approx k_1 > k_6 \approx k_7$  in 100% MeOH, 100% EtOH, and 80% EtOH but not in 70% TFE<sup>[7,9]</sup>. The rate ratios for 1, 3, 4, and 5 in 100% MeOH, 100% EtOH, and 80% EtOH are close to unity ( $k_{ROCOF}/k_{EtOCOFOF} = 0.93 \sim 1.1$ ), suggesting that electronic and/or steric influences due to the presence of a branching  $\beta$ -alkyl group in the alkyl fluoroformates can be neglected<sup>[7]</sup>. The specific rates for the solvolyses of 7 in 100% MeOH, 100% EtOH, and 80% EtOH are similar to the values for 6. However, the steric influence of alkyl group increases, and the specific rate of 7 in 70% TFE is somewhat faster than the rates of 1, 3, 4, 5, and 6. The higher rate ratio ( $k_{t-BuOCOFOF}/k_{EtOCOFOF} = 10$ ) in 70% TFE relative to those in 100% MeOH, 100% EtOH, and 80% EtOH probably results because the solvolysis of 7 (via the relatively stable *t*-butyl cation)<sup>[7(e)]</sup> is more favored by the electrophilic influence of relatively acidic TFE than the other alkyl fluoroformates, which are believed to proceed by a bimolecular pathway.

TABLE III A COMPARISON OF THE SPECIFIC RATES ( $10^4 k, s^{-1}$ )<sup>a</sup>, AND KINETIC SOLVENT ISOTOPE EFFECT VALUES (KSIES,  $k_{MeOH}/k_{MeOD}$ ) FOR THE SOLVOLYSES OF SEVERAL ALKYL FLUOROFORMATES (ROCOF) IN PURE AND MIXED SOLVENTS AT 40.0°C

Solvent <sup>b</sup>	R= Me <sup>d</sup>	3 <sup>e</sup>	4 <sup>f</sup>	5 <sup>g</sup>	1 <sup>h</sup>	6 <sup>i</sup>	7 <sup>j</sup>
100% MOH	5.81	2.32	2.19	2.15	2.25	0.595	0.528
100% EtOH	1.09	0.394	0.437	0.378	0.405	0.0968	0.0934
80% EtOH	43.6	14.3	14.0	14.4	13.3	3.93	3.69
70% TFE	10.8	3.61	2.20	2.33	1.83	0.779	37.1
$(k_{MeOH}/k_{MeOD})^c$	3.98	3.10	3.32	3.40	3.40	2.53	1.26

<sup>a</sup> Values obtained using Arrhenius plots with the specific rates reported at different temperatures. <sup>b</sup> See footnotes to Table 1. <sup>c</sup> Specific rate ratio of solvolysis of 1 in MeOH and MeOD. <sup>d</sup> Methyl fluoroformate (ref. 9). <sup>e</sup> From ref. 7(a). <sup>f</sup> From ref. 7(b). <sup>g</sup> From ref. 7(c). <sup>h</sup> This study. <sup>i</sup> From ref. 7(d). <sup>j</sup> From ref. 7(e).

The KSIE value ( $k_{MeOH}/k_{MeOD} = 3.40$  at 45.0 °C) for methanolysis of 1 is of a magnitude usually taken to indicate that nucleophilic attack by a methanol molecule is assisted by general-base catalysis by a second methanol molecule (Table 3)<sup>[10]</sup>. The KSIE value for 1 is slightly larger than for the methanolysis of 2 ( $k_{MeOH}/k_{MeOD} = 1.77$  at 45.0 °C)<sup>[5]</sup>, which further supports the proposal that bond formation is more advanced in the transition state for addition to fluoroformate than to chloroformate.

Activation parameter values for solvolyses of 1 and 2 in four solvents are tabulated in Table 2. The values of the enthalpy and entropy of activation for the solvolysis of 1 are 8.8 ~ 12.0 Kcal mol<sup>-1</sup> and -37.4 ~ -45.1 cal mol<sup>-1</sup> K<sup>-1</sup>, respectively. The same values for the solvolysis of 2 are 12.9 ~ 20.0 Kcal mol<sup>-1</sup> and -15.8 ~ -38.8 cal mol<sup>-1</sup> K<sup>-1</sup>, respectively. The large negative entropies of activation are consistent with the bimolecular nature of the rate-determining step<sup>[11]</sup>. A bimolecular mechanism is strongly indicated by the slower reactions in TFE-rich solvents and by the appreciably negative entropies of activation. However, it has not yet been established whether the process involves a stepwise addition-elimination (association-dissociation) or a concerted (S<sub>N</sub>2) pathway. The original and extended G-W equations [Equations (1) and (2)] give information that is very helpful in assessing the mechanism of solvolysis reactions.

Analysis of the 18 specific rates of Table 1 in terms of the original G-W Equation (1) led to an extremely poor correlation coefficient (*R*) of 0.090. As shown in Figure 1, the plot corresponding to this correlation showed that the four data points for solvolyses in binary TFE-ethanol solvents have moderate to appreciable deviation from the linear plot. This was previously discussed in detail using the extended G-W Equation (2) for the specific rates of solvolysis of alkyl and acyl haloformate esters in binary TFE-ethanol solvents<sup>[7,12]</sup>. Analysis in terms of the extended G-W Equation (2) for the specific rates of solvolysis of 1 in all the solvents gave an acceptable linear correlation with values of 1.84 for *l*, 0.84 for *m*, -0.05 for *c* (residual term), and 0.925 for the correlation coefficient. Recalculation with omission of TFE-ethanol mixture data gave a very good linear correlation with values of 1.63 for *l*, 0.78 for *m*, -0.01 for *c*, and 0.980 for the correlation coefficient (*R*). The relative magnitudes of *l* and *m* (*l/m* ratio) have often been suggested as useful mechanistic criteria. As shown in Table 4, the *l/m* ratio is divided into two classes. Entries postulated to be associated with the addition-elimination (A-E) mechanism have values of 1.7 ~ 2.8 while those believed to be associated with the ionization (I) mechanism have values of 0.44 ~ 0.63. The *l* and *m* values of 1 are similar to those reported previously for other primary and secondary alkyl fluoroformates. In Figure 2, a plot of  $\log(k/k_0)$  for 1 against  $\log(k/k_0)$  for *n*-octyl fluoroformate<sup>[13]</sup> shows good linear correlation [*i.e.*,  $\log(k/k_0)_{NeopOCOFOF} = 0.97 \log(k/k_0)_{n-OctOCOFOF} + 0.11$ , *R* = 0.991] in pure and mixed solvents. These phenomena provide strong evidence for a similarity model. The higher *m*-value for the solvolyses of 1 relative to 2 may reflect the kinetically favorable influence of the increased solvation on the developing positive charge on the carbonyl carbon in the presence of the more electronegative fluorine attached at the

carbonyl carbon <sup>[7]</sup>. As shown in Table 4, the solvolyses of primary and secondary alkyl fluoroformates in all the solvents studied were found to proceed through only an addition-elimination mechanism [Equation (3)]. The addition step is rate-determining, despite the increasing chain length in primary alkyl fluoroformates (1, 3, 4, 5, and *n*-OctOCOF) and the influence of a branched-chain alkyl group as in 6 <sup>[7, 13]</sup>.

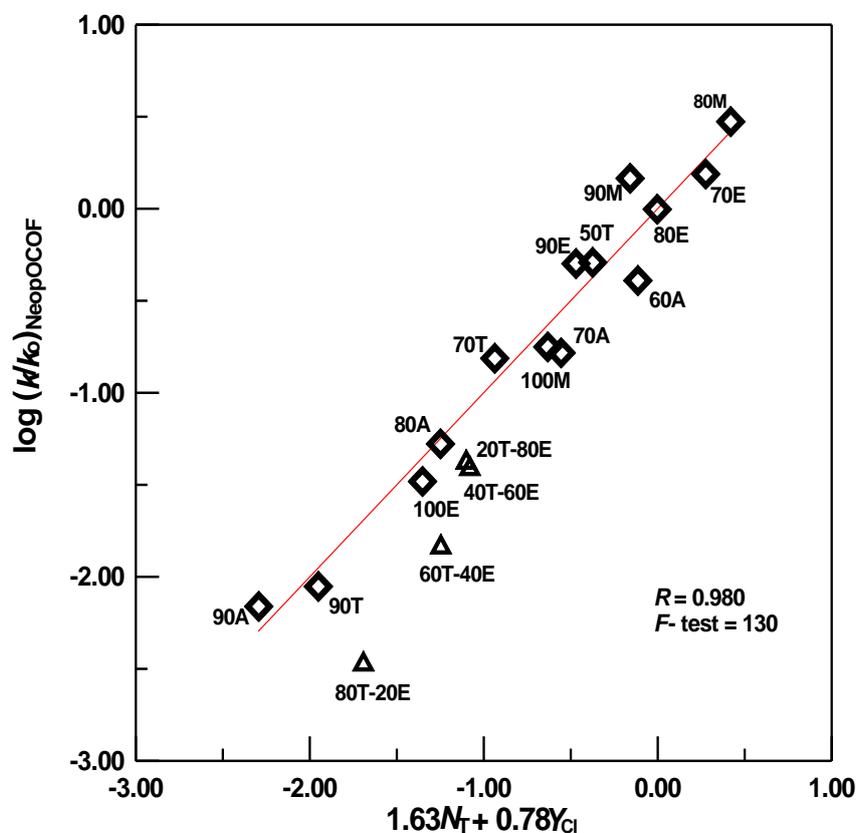


Figure 1 Plot of  $\log(k/k_0)$  for the solvolyses of neopentyl fluoroformate (1) at 45.0°C against  $(1.63N_T + 0.78Y_{C1})$ . Data points for the TFE-ethanol mixtures are not included in the correlation.

TABLE IV CORRELATIONS OF THE SPECIFIC RATES OF SOLVOLYSES OF 1 AND A COMPARISON WITH CORRESPONDING VALUES FOR THE SOLVOLYSES OF OTHER ALKYL HALOFORMATE ESTERS USING THE EXTENDED G-W EQUATION

Substrate	$n^a$	$l^b$	$m^b$	$c^b$	$R^c$	$l/m$	Mech. <sup>d</sup>
NeopOCOF (1) <sup>e</sup>	18		$0.05 \pm 0.13$	$-0.93 \pm 0.22$	0.090		
	18	$1.84 \pm 0.20$	$0.84 \pm 0.10$	$-0.05 \pm 0.13$	0.925	2.19	A-E
	14 <sup>f</sup>	$1.63 \pm 0.10$	$0.78 \pm 0.05$	$-0.01 \pm 0.07$	0.980	2.09	A-E
NeopOCOCI (2)	13 <sup>g</sup>	$1.76 \pm 0.14$	$0.48 \pm 0.06$	$0.14 \pm 0.08$	0.977	3.67	A-E
	8 <sup>g</sup>	$0.36 \pm 0.10$	$0.81 \pm 0.14$	$-2.79 \pm 0.33$	0.938	0.44	I
EtOCOF (3)	17 <sup>h</sup>	$1.34 \pm 0.14$	$0.77 \pm 0.07$	$-0.06 \pm 0.10$	0.942	1.74	A-E
<i>n</i> -PrOCOF (4)	16 <sup>i</sup>	$1.72 \pm 0.12$	$0.91 \pm 0.07$	$0.05 \pm 0.08$	0.970	1.89	A-E
<i>i</i> -BuOCOF (5)	18 <sup>j</sup>	$1.68 \pm 0.07$	$0.80 \pm 0.04$	$0.01 \pm 0.05$	0.989	2.10	A-E
<i>i</i> -PrOCOF (6)	20 <sup>k</sup>	$1.59 \pm 0.16$	$0.80 \pm 0.06$	$0.06 \pm 0.08$	0.957	1.99	A-E
<i>i</i> -PrOCOCI	20 <sup>l</sup>	$0.28 \pm 0.05$	$0.52 \pm 0.03$	$-0.12 \pm 0.05$	0.979	0.54	I
<i>t</i> -BuOCOF (7)	17 <sup>m</sup>	$0.41 \pm 0.05$	$0.65 \pm 0.03$	$0.02 \pm 0.04$	0.989	0.63	I
<i>n</i> -OctOCOF	19 <sup>n</sup>	$1.67 \pm 0.07$	$0.76 \pm 0.03$	$-0.08 \pm 0.18$	0.988	2.20	A-E
1-AdOCOF	10 <sup>o</sup>	$2.78 \pm 0.21$	$1.01 \pm 0.06$	$0.09 \pm 0.16$	0.978	2.78	A-E
	16 <sup>o</sup>	~	$0.70 \pm 0.01$	$-0.02 \pm 0.05$	0.999	~0	I

<sup>a</sup> Number of solvent systems included in the correlation. <sup>b</sup> Using equation (2), with standard errors for  $l$  and  $m$  values and with standard errors of the estimate accompanying the  $c$  values. <sup>c</sup> Correlation coefficient. <sup>d</sup> Addition-elimination (A-E) and ionization (I). <sup>e</sup> This study; <sup>f</sup> Omitting the TFE-ethanol solvents; <sup>g</sup> The 21 solvent systems divided into 8 aqueous fluoroalcohol solvents and the remainder (ref. 5). <sup>h</sup> From ref. 7 (a). <sup>i</sup> From ref. 7 (b). <sup>j</sup> From ref. 7 (c). <sup>k</sup> From ref. 7 (d). <sup>l</sup> From ref. 6 (d). <sup>m</sup> From ref. 7 (e). <sup>n</sup> From ref. 13. <sup>o</sup> From ref. 7 (f).

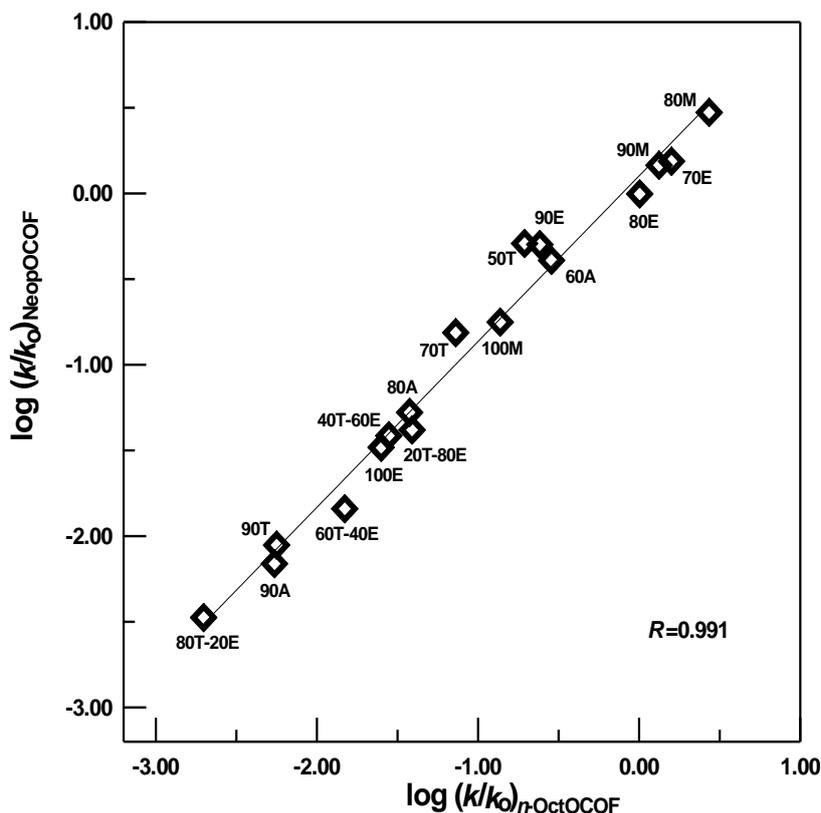


Figure 2 Plot of  $\log(k/k_0)$  for the solvolyses of neopentyl fluoroformate (1) at 45.0°C against  $\log(k/k_0)$  for the solvolyses of *n*-octyl fluoroformate at 24.2°C<sup>[13]</sup>

Consideration of the fluoride/chloride ratio ( $k_F/k_{Cl}$ ) in nucleophilic substitution reactions has long been recognized as a useful tool for studying reaction mechanism<sup>[14]</sup>. For the ionization pathway, the  $k_F/k_{Cl}$  values of about  $10^{-5}$  for *tert*-butyl halide solvolyses<sup>[15]</sup>, about  $10^{-4}$  for acetyl halide solvolyses<sup>[15]</sup>, and about  $10^{-5}$  for 1-adamantyl haloformate solvolyses<sup>[6(e), (f)]</sup> have been reported. Since the carbon-fluoride bond (C-F) is much stronger than the carbon-chloride bond (C-Cl), if the carbon-halogen bond is broken in the rate-determining step (ionization pathway), the  $k_F/k_{Cl}$  ratio is expected to exhibit a significant leaving group effect. In contrast, if the addition step is rate-determining (*i.e.*, bimolecular pathway), values of close to unity, reflecting a large electron deficiency at the carbonyl carbon of the fluoroformate, are frequently observed. A previous report concerning the solvolyses of 3, 4, 5, 6, and *n*-octyl haloformate<sup>[7, 13]</sup>, which are believed to solvolyse by an addition-elimination mechanism. The study found a  $k_F/k_{Cl}$  ratio of somewhat below unity in ethanol and methanol and slightly greater than unity for solvolyses in mixtures of water with ethanol, methanol, acetone, or TFE<sup>[7]</sup>. For other haloformate esters,  $k_F/k_{Cl}$  ratios of 1.09 to 7.16 have been reported for solvolyses in 70% aqueous acetone at 30.1 °C<sup>[16]</sup>. As shown in Table 1, the  $k_F/k_{Cl}$  ratios of solvolysis of 1 and 2 were similar to those reported previously for other primary and secondary alkyl haloformates that have been reported to proceed through a bimolecular pathway. The  $k_F/k_{Cl}$  ratios are smaller for the 1-adamantyl substrates, which presumably proceed through a solvolysis-decomposition reaction (ionization pathway) in ethanol, methanol, and 80% ethanol.

### III. CONCLUSIONS

The solvolyses of 1 give a satisfactory extended G–W correlation over a wide range of  $N_T$  and  $Y_{Cl}$  values. The sensitivities to changes in  $N_T$  and  $Y_{Cl}$  ( $l=1.63$ ,  $m=0.78$ ) are very similar to those for several fluoroformate esters (Table 4). Fluoroformate esters have been shown to solvolyse by an addition–elimination pathway with a rate-determining addition step. The  $k_F/k_{Cl}$  values obtained by comparison with the corresponding solvolysis of 2 are similar to those for the solvolyses of 3, 4, 5, and 6, consistent with a bimolecular addition–elimination mechanism that proceeds through a tetrahedral intermediate [Equation (3)]. The KSIE value for methanolysis of 1,  $k_{MeOH}/k_{MeOD} = 3.40$ , is of a magnitude usually taken to indicate that nucleophilic attack by a methanol molecule is assisted by general-base catalysis by a second methanol molecule. The large negative entropies of activation ( $-37.2$  to  $-45.1$  cal mol<sup>-1</sup> K<sup>-1</sup>) for the solvolyses of 1 in four solvents are consistent with the bimolecular nature of the rate-determining step. Unlike the solvolyses of 2, in which two reaction channels were observed, the solvolyses of 1 in this study proceeded through only an addition-elimination pathway with the addition step as rate determining [Equation (3)].

### IV. EXPERIMENTAL

Neopentyl fluoroformate (1, 55~57°C/120 mmHg) was prepared from neopentyl alcohol (Aldrich, 10.0 g, 0.11 mol) via 1-chloroethyl chloroformate (TCI, 17.0 g, 0.12 mol) by a procedure described earlier<sup>[17]</sup>. Solvent were purified as previously

described <sup>[7(e)]</sup>. The kinetic procedures were described earlier <sup>[7(e)]</sup>. A substrate concentration of about  $5.86 \times 10^{-3}$  mol dm<sup>-3</sup> was used and 5 mL portions were removed for titration, although 2 mL portions were run in the TFE-H<sub>2</sub>O and TFE-EtOH mixtures. The *l* and *m* values were calculated using commercially available computer programs for multiple regression analyses.

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