Correlation of the Rates of Solvolysis of Isopropyl Fluoroformate Using the Extended Grunwald-Winstein Equation

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The specific rates of solvolysis of isopropyl fluoroformate are well correlated using the extended Grunwald-Winstein equation, with a sensitivity (l) to changes in solvent nucleophilicity (N_T) and a sensitivity (m) to changes in solvent ionizing power (Y_{Cl}). The sensitivities ($l = 1.59 \pm 0.16$ and $m = 0.80 \pm 0.06$) toward changes in solvent nucleophilicity and solvent ionizing power, and the k_F/k_{Cl} values are very similar to those for solvolyses of n-octyl fluoroformate, suggesting that the addition step of an addition-elimination mechanism is rate-determining. For methanolysis, a solvent deuterium isotope effect of 2.53 is compatible with the incorporation of general-base catalysis into the substitution process. The large negative values for the entropies of activation are consistent with the bimolecular nature of the proposed rate-determining step. These observations are also compared with those previously reported for the corresponding chloroformate and fluoroformate esters.

Key Words : Isopropyl fluoroformate, Addition-elimination, Grunwald-Winstein equation
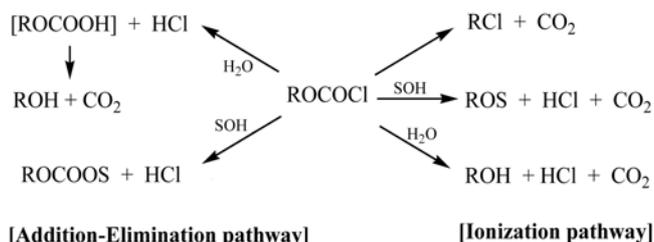
Introduction

The extended Grunwald-Winstein equation (eqn. 1) has proven extremely valuable in studies of the mechanism of solvolysis reaction.[1,2] In eqn. (1), k and k_o are the specific rates of solvolysis of a

$$\log(k/k_o) = lN_T + mY_{Cl} + c \qquad (1)$$

substrate RX in a given solvent and in the standard solvent (80% ethanol), respectively; l represents the sensitivity of the solvolysis to changes in solvent nucleophilicity N_T;[2,3] m represents the sensitivity of the solvolysis to changes in solvent ionizing power Y_{Cl};[4,5] c represents a constant (residual) term. Scales of solvent nucleophilicity and of solvent ionizing power are available and, by measuring k and k_o, 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, and, for a reaction proceeding with extensive nucleophilic assistance, the l value will be in the region of 1.6 to 2.0 and the m value in the region below 0.6.[5(d),(e),6] Accordingly, determination of these values will be a valuable source of information concerning the structure of the transition state for these solvolyses.

The simplest secondary alkyl group, isopropyl chloroformate,[6] leads to solvolyses which continue to show the two competing reaction channels. In this case, an ionization pathway dominates over a wide range of solvents and only in the more nucleophilic and least ionizing solvents is the addition-elimination pathway dominant (Scheme 1).

The ionization pathway with solvolysis-decomposition is the only one operating for solvolyses of 1-adamantyl chloroformate.[7,8] Loss of carbon dioxide leads to the relatively stable 1-adamantyl cation, which can be captured by simul-

Scheme 1

taneously formed chloride ion or solvent. The corresponding 1-adamantyl fluoroformate[9] showed a very much reduced tendency toward ionization and only in solvents of high ionizing power and low nucleophilicity dose the behavior parallel that of the chloroformate. In other solvents, the predominant pathway involves addition-elimination.

A comparison of leaving group effects on the rates of solvolysis of chloroformate and fluoroformate esters might provide useful information about the reaction mechanisms.[10] For a recent report concerning the solvolyses of the n-octyl[11] and benzyl fluoroformate,[12] the addition-elimination pathway was observed over the full range of solvents and the k_F/k_{Cl} ratios were only slightly below or above unity.

In the present paper, we report on the overall specific rates for solvolysis of isopropyl fluoroformate in a variety of pure and binary solvents and these analyses are then combined with a consideration of leaving group effects to arrive at a reasonable mechanism. In addition to the application of the extended Grunwald-Winstein equation to the specific rates, the influence of temperature on the specific rate (for four solvents) allows enthalpies and entropies of activation to be calculated, a measurement in methanol-d allows a determination of the solvent deuterium isotope effect.

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Table 1. Specific rates of solvolysis of isopropyl fluoroformate in a variety of pure and mixed solvents at 40.0 °C and the N_T and Y_{Cl} values for the solvents, and the specific rate ratio relative to isopropyl chloroformate (k_F/k_{Cl})

Solvent (%)[a]	$10^4 k$, s^{-1}	N_T[b]	Y_{Cl}[c]	k_F/k_{Cl}[d]
100 MeOH[e]	0.595 ± 0.021	0.17	−1.17	0.39
90 MeOH	5.40 ± 0.22	−0.01	−0.18	1.76
80 MeOH	11.8 ± 0.01	−0.06	0.67	2.37
70 MeOH	18.4 ± 0.1	−0.40	1.46	2.40
60 MeOH	25.2 ± 0.4	−0.54	2.07	2.10
100 EtOH	0.0968 ± 0.0030	0.37	−2.52	0.18
90 EtOH	1.82 ± 0.02	0.16	−0.94	1.68
80 EtOH	3.93 ± 0.21	0.00	0.00	2.11
70 EtOH	6.40 ± 0.07	−0.20	0.78	2.04
60 EtOH	9.16 ± 0.04	−0.38	1.38	1.79
50 EtOH	14.9 ± 1.0	−0.58	2.02	1.55
90 Me$_2$CO	0.0366 ± 0.0034	−0.35	−2.39	0.34
80 Me$_2$CO	0.224 ± 0.010	−0.37	−0.83	0.53
70 Me$_2$CO	0.724 ± 0.001	−0.42	0.17	0.61
60 Me$_2$CO	1.84 ± 0.08	−0.52	0.95	0.64
70 TFE	0.779 ± 0.015	−1.98	2.96	0.067
50 TFE	2.66 ± 0.41	−1.73	3.16	−
60T-40E[f]	0.0915 ± 0.0022	−0.94	0.63	0.12
40T-60E[f]	0.141 ± 0.013	−0.34	−0.48	0.38
20T-80E[f]	0.217 ± 0.010	0.08	−1.42	0.69

[a]Volume/volume basis at 25.0 °C, except for TFE-H$_2$O mixtures, which are on a weight/weight basis. [b]Values from refs. 2, 3. [c]Values from refs. 4, 5. [d]Values relative to those for the corresponding solvolysis of isopropyl chloroformate (values from ref. 6). [e]Value in 100% MeOD of 0.235 (± 0.02) × 10^{-4} s^{-1}, leading to a k_{MeOH}/k_{MeOD} value of 2.53, and the value of isopropyl chloroformate, $k_{H_2O}/k_{D_2O} = 1.25$. [f]T-E represents TFE-ethanol mixtures.

Results

The specific rates of solvolysis of isopropyl fluoroformate at 40.0 °C are reported in Table 1. The solvents consisted of ethanol, methanol, binary mixtures of water with ethanol, methanol, 2,2,2-trifluoroethanol (TFE), acetone, and three binary mixtures of TFE and ethanol. The N_T and Y_{Cl} values are also reported in Table 1, together with the k_F/k_{Cl} ratios. A determination was also made in methanol-*d* (MeOD, footnote to Table 1).

For methanol, 80% methanol, ethanol, 80% ethanol, and 70% TFE, specific rates of solvolysis were determined at two and three additional temperatures, and these values, together with calculated enthalpies and entropies of activation, are reported in Table 2.
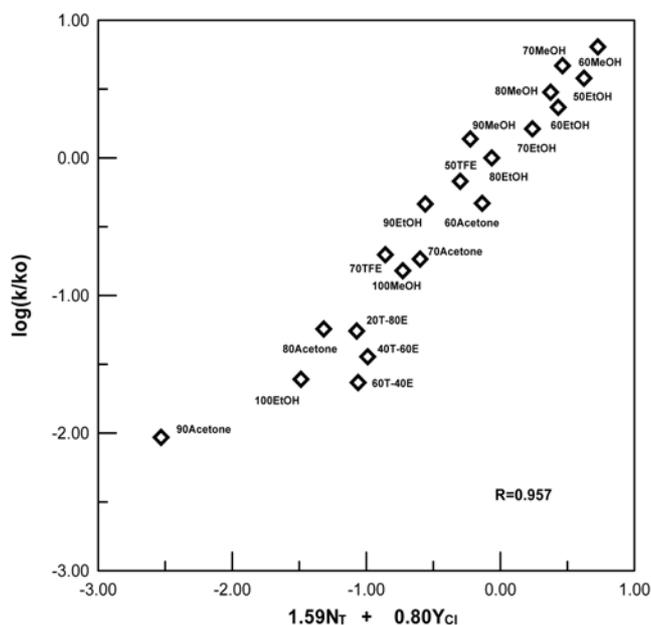
Discussion

A useful tool for quantitatively estimating the rate-controlling influence of nucleophilic participation by solvent during a solvolysis reaction involves the application of the extended Grunwald-Winstein equation (eq. 1)[1,2] and compares the *l* and *m* values with those previously obtained for other haloformate esters.[12]

A consideration in terms of the simple Grunwald-Winstein equation [eqn. (1) without the lN_T term] to the specific rates of solvolysis in 20 representative solvents at 40.0 °C leads to

Table 2. Specific rates for solvolysis of isopropyl fluoroformate at various temperatures and enthalpies and entropies of activation

Solvent (%)[a]	T, °C	$10^4 k$, s^{-1}	$\Delta H^{\neq}_{313.15\,°C}$[b] (kcal mol^{-1})	$\Delta S^{\neq}_{313.15\,°C}$[b] (cal mol^{-1}K^{-1})
100% MeOH	30.0	0.300 ± 0.020	11.7 ± 0.7	−40.8 ± 2.5
	40.0	0.595 ± 0.021		
	45.0	0.842 ± 0.062		
	50.0	1.03 ± 0.03		
80% MeOH	30.0	6.94 ± 0.71	8.9 ± 0.3	−43.7 ± 1.1
	40.0	11.8 ± 0.01		
	50.0	18.4 ± 0.9		
100% EtOH	30.0	0.0555 ± 0.0052	11.3 ± 0.9	−45.5 ± 3.4
	40.0	0.0968 ± 0.0030		
	45.0	0.150 ± 0.006		
	50.0	0.182 ± 0.031		
80% EtOH	30.0	2.25 ± 0.30	9.5 ± 0.2	−43.9 ± 0.6
	40.0	3.93 ± 0.21		
	45.0	5.02 ± 0.09		
	50.0	6.36 ± 0.11		
70% TFE	30.0	0.360 ± 0.050	14.0 ± 0.04	−32.8 ± 0.2
	40.0	0.779 ± 0.015		
	45.0	1.13 ± 0.06		

[a]Volume-volume basis at 25.0 °C. [b]With associated standard error.

Figure 1. Plot of log(k/k_o) for solvolyses of isopropyl fluoroformate in all of the solvents at 40.0 °C against ($1.59N_T + 0.80Y_{Cl}$).

a poor correlation with value of 0.653 for the correlation coefficient (R). Again, An analysis using the extended Grunwald-Winstein equation of the data for the specific rates of solvolysis of isopropyl fluoroformate leads to a good linear correlation with values of 1.59 ± 0.16 for *l*, 0.80 ± 0.06 for *m*, 0.06 ± 0.08 for *c*, and 0.957 for the correlation coefficient (F-test = 93). Inspection of the plot corresponding to this correlation (Figure 1) showed that the three data points for solvolyses in TFE-ethanol mixtures lay below the best fit line. Recalculation with omission of these points led to
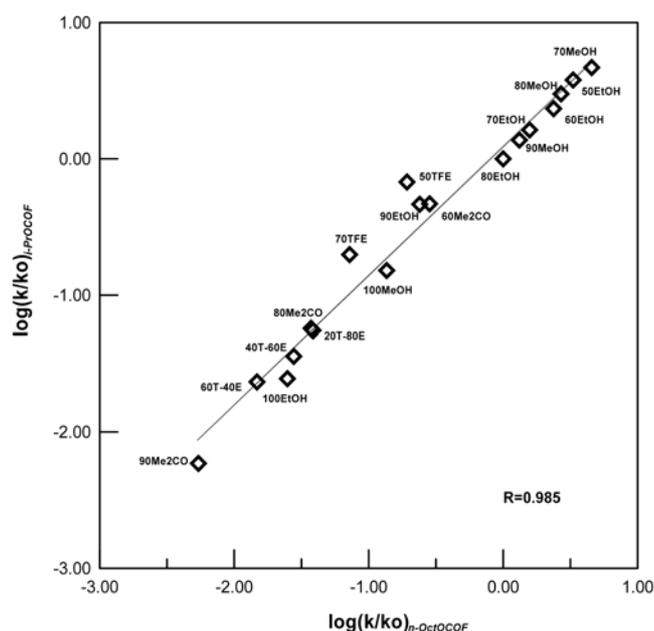
Figure 2. Plot of $\log(k/k_o)$ for solvolyses of isopropyl fluoroformate against $\log(k/k_o)$ for solvolyses of *n*-octyl fluoroformate in all of the solvents [$\log(k/k_o)_{i\text{-PrOCOF}} = 0.95 \log(k/k_o)_{n\text{-OctOCOF}} + 0.097$].

values of 1.44 ± 0.12 for l, 0.74 ± 0.04 for m, -0.03 ± 0.06 for c, and 0.978 for the correlation coefficient (F-test = 152). In earlier correlations of other haloroformate esters, it was found that the data points for these solvent systems usually lay below the correlation line.[5(d),13,14] This phenomenon was very recently discussed[15] and it will not be considered again in this type. Correlations were carried out both with and without the TFE-ethanol data. The results of the correlation are presented in Figure 1 and reported in Table 3, together with the corresponding parameters obtained in the analyses of earlier studied substrates.

The sensitivity to changes in solvent nucleophilicity (l) will be close to unity, or even higher, if covalent attachment of solvent, functioning as a nuclephile, is involved in the slow step. The l and m values of 1.59 and 0.80 for the solvolysis of isopropyl fluoroformate, respectively, were

very similar to previous values reported for bimolecular solvolyses of other chloroformate and fluoroformate esters, believed to solvolyze by an addition-elimination mechanism, with the addition being rate-determining.

A plot of $\log(k/k_o)$ for isopropyl fluoroformate against $\log(k/k_o)$ for *n*-octyl fluoroformate[11] is shown in Figure 2. This shows a good linear correlation (R = 0.985) in pure and mixed solvents. A good linear relationship for the solvolyses of isopropyl fluoroformate and *n*-octyl fluoroformate gives a strong evidence for a similarity model.

The l and m ratios have also been suggested as a useful mechanistic criterion and the values of Table 3 divide into two classes with values of 1.9 to 3.0 for those entries postulated to represent addition-elimination pathway and values below 0.8 for those believed to represent ionization pathway.[6,7,13] For isopropyl fluoroformate, the value for the ratio of 2.0 is very similar to those previously observed for the solvolyses of *n*-octyl fluoroformate[11] and benzoyl fluoride,[16] 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.

The study of both the fluoroformate and chloroformate esters provides a route to mechanistic deductions in terms of the k_F/k_{Cl} ratios.[18] This is especially so when the attack is at an acyl carbon. When the carbon-halogen bond is broken in a nucleophilic displacement reaction, the specific rates of fluoro-derivative react appreciably slower than that for chloro-derivative, as much as 10^5 to 10^7 times slower for a unimolecular ionization[18,19] and some 10^1 to 10^3 times slower in bimolecular displacements at a saturated carbon.[20] The previous observations that, when a bimolecular attack at an acyl carbon is operative, fluoroformate and chloroformate esters solvolyze at very similar rates, frequently with the fluoroformate ester the faster, have been uniformly rationalized in terms of the addition step of an addition-elimination mechanism being rate determining. The k_F/k_{Cl}

Table 3. Coefficients from extended Grunwald-Winstein[a] correlations of the solvolyses of isopropyl fluoroformate and a comparison with corresponding values for the solvolyses of other chloroformate and fluoroformate esters and benzoyl fluoride

Substrate	Mech[b]	n^c	l^d	m^d	c^d	R^e	l/m
PhOCOCl[f]	A-E	21	1.68 ± 0.10	0.57 ± 0.06	0.12 ± 0.41	0.973	2.95
MeOCOCl[g]	A-E	19	1.59 ± 0.09	0.58 ± 0.05	0.16 ± 0.17	0.977	2.74
EtOCOCl[h]	A-E	28	1.56 ± 0.09	0.55 ± 0.03	0.19 ± 0.24	0.967	2.84
EtOCOCl[h]	I	7	0.69 ± 0.13	0.82 ± 0.16	-2.40 ± 0.27	0.946	0.84
i-PrOCOCl[i]	I	20	0.28 ± 0.05	0.52 ± 0.03	-0.12 ± 0.05	0.979	0.54
i-PrOCOF[j]	A-E	20	1.59 ± 0.16	0.80 ± 0.06	0.06 ± 0.08	0.957	1.99
OctOCOF[k]	A-E	23	1.80 ± 0.13	0.79 ± 0.06	0.13 ± 0.34	0.959	2.28
C_6H_5COF[l]	A-E	41	1.58 ± 0.09	0.82 ± 0.05	-0.09 ± 0.10	0.953	1.93
1-AdOCOCl[m]	I	15	~0	0.47 ± 0.03	0.03 ± 0.05	0.985	~0

[a]Using equation 1. [b]Addition-elimination (A-E) and ionization (I). [c]Number of solvent systems included in the correlation. [d]With associated standard errors, those associated with the c values being the standard errors of the estimate. [e]Correlation coefficient. [f]Values from ref. 14. [g]Values from ref. 17. [h]Values from ref. 13. [i]Values from ref. 6 and the 24 solvents systems studied, with omission of EtOH, 90%EtOH, MeOH, and 90%MeOH. [j]This study [k]Values from ref. 11. [l]Values from ref. 16. [m]Values from ref. 7.

ratios for S_N1 solvolyses have been observed to be in the range of 10^{-6} (for Ph_3CX[21]) to 10^{-7}(for p-$Me_2NC_6H_4COX$[19]) and a low value of 1.3×10^{-4} was also observed for acetyl halide solvolyses in 75% acetone.[18] These values reflect an appreciable ground-state stabilization for the fluoride[22] 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, reflecting a large electron deficiency at the carbonyl carbon of a haloformate incorporating fluorine,[16] are frequently observed. This situation has recently been discussed in a consideration of n-octyl haloformate solvolyses,[11] where k_F/k_{Cl} specific rate ratios of 0.6 to 15 were observed. Due to the previous study of isopropyl chloroformate[6] involving 19 of the 20 solvent compositions of the present study, a wide range of k_F/k_{Cl} values are available. For a meaningful consideration of this specific rate ratio at 40.0 °C for solvolyses of isopropyl fluoroformate and isopropyl chloroformate (Table 1), it is important that the k_F and k_{Cl} values are for the same reaction pathway. The values for the ratio vary from a low of 0.2 in 100% ethanol (similar to the 0.6 for n-octyl haloformate) to a high of 2.1 in 80% ethanol (similar to the 2.9 for n-octyl haloformate in 80% acetone). The low value for 70% TFE is to be expected because of the previously demonstrated[9] dominance of an ionization pathway for solvolysis of the chloride in this solvent.

The solvent isotope effect has previously been studied for several solvolyses of chloroformate esters. In pure water, the k_{H_2O}/k_{D_2O} ratio was in the range of 1.79 to 1.89 for methyl, ethyl, and phenyl chloroformate believed to react by the bimolecular mechanism.[23,24] The value for isopropyl chloroformate,[6] in the ionization range, was somewhat lower at 1.25 and the value for diphenylcarbamoyl chloride was lower again at 1.1.[23] Values in the range predicted for a bimolecular solvolysis have recently been reported for k_{MeOH}/k_{MeOD} of 2.1-2.5 for a series of substituted phenyl chloroformates[25,26] and 2.4 for p-nitrobenzyl chloroformate.[5(d)] The value (footnote to Table 1) for methanolysis of isopropyl fluoroformate of $k_{MeOH}/k_{MeOD} = 2.53$ 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.[27,28]

For solvolyses in methanol, 80% methanol, ethanol, 80% ethanol, and 70%TFE, the values of the enthalpy and the entropy of activation for the solvolysis of isopropyl fluoroformate (Table 2) are 9.3 to 14.0 kcal mol^{-1} and -32.7 to -45.5 cal mol^{-1}K^{-1}, respectively. These values are consistent with the finding by Orlov[29] of similar activation parameters for the ethanolyses of methyl, ethyl and isopropyl chloroformates and ethyl chlorothioformate. The very negative entropies of activation are consistent with the bimolecular reaction of the proposed rate-determining step.

Conclusions

The specific rates of solvolyses of isopropyl fluoroformate give good correlation when analyzed using the extended

Grunwald-Winstein equation over the full range of solvents. The sensitivities to changes in N_T and Y_{Cl} ($l = 1.59$ and $m = 0.80$) are very similar to those for several fluoroformate and chloroformate esters (Table 3), which have been shown to solvolyze with the addition step of an addition-elimination pathway being rate determining.

The k_F/k_{Cl} values obtained in a comparison with the corresponding solvolysis of isopropyl fluoroformate are similar to those for solvolyses of n-octyl fluoroformate, consistent with a bimolecular addition-elimination mechanism, proceeding through a tetrahedral intermediate. Favoring the explanation in terms of alkyl variation is the observation[30] that the k_F/k_{Cl} ratio for solvolyses of haloformate esters in 70% acetone at 30.1 °C decreases from methyl (7.16), ethyl (5.46) or n-propyl (4.95) to isopropyl (the k_F/k_{Cl} ratio of isopropyl group in 70% acetone at 40.0 °C is 0.61), suggesting that a value of lesser than unity would indeed be upon incorporation of a bulky secondary alky group. This trend could possibly be governed by increasing steric effects.

The solvent deuterium isotope effect value for methanolysis, $k_{MeOH}/k_{MeOD} = 2.53$ 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 entropies of activation (-32.7 to -45.5 cal mol^{-1}K^{-1}) for isopropyl fluoroformate reaction, believed to involve rate-determining attack at acyl carbon, are considerably more negative than the values for reactions believed to proceed by an ionization pathway (the entropies of activation for 1-adamantyl chloroformate are $+3.3$ to $+6.7$ cal mol^{-1}K^{-1}). The values of more negative entropy of activation for isopropyl fluoroformate reaction are consistent with the bimolecular nature of the rate-determining step.

Unlike the solvolyses of isopropyl chloroformate, where, in most solvents, a solvolysis-decomposition (ionization pathway) was observed, the solvolyses of isopropyl fluoroformate follow a pathway involving bimolecular attack by solvent at acyl carbon, by what is suggested that the addition step of an addition-elimination pathway is rate determining.

Experimental

Isopropyl chloroformate in toluene (38.56 mL, 0.038 mol) was syringed into a three-neck flask (250 mL) containing dried KF (2.94 g, 0.05 mol) and 18-crown-6 (0.36 g, 0.0013 mol) and fitted with a Teflon stirring bar, a condenser topped by an N_2 gas inlet, a septum cap, and a ground glass stopper, as described earlier.[30] 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 1729 cm^{-1}; fluoroformate C=O stretch at 1825 cm^{-1}). After total reaction time 48 hour, the product fluoroformate was isolated directly from the reaction apparatus by simple distillation at a reaction temperature of 80-83 °C.

Solvents were purified and the kinetic runs carried out as previously described.[9,31] All runs were performed using a

substrate concentration of 5.128×10^{-3} *M* and with 5 mL portions removed for titration, but with 2 mL portions for runs in TFE-H_2O and TFE-EtOH mixtures.

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