

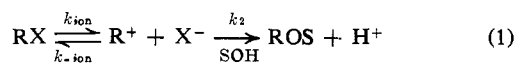
Table I. k_1^0 and α Values for the Solvolysis of 4-Br at 35°

$10^4[4\text{-Br}]$, mol l. ⁻¹	$10^2[2,6\text{-Lutidine}]$, mol l. ⁻¹	% TFE (w/w) in TFE- H ₂ O	$10^5 k_1^0$, sec ⁻¹	α , mol ⁻¹
1.57	12.3	100	4.13 ± 0.23	394 ± 42
1.73	7.1	97	3.70 ± 0.20	225 ± 33
1.57	12.3	90	3.30 ± 0.02	110 ± 5
1.68	6.6	80	3.40 ± 0.03	27 ± 2
1.65	6.5	70	3.51 ± 0.02	11 ± 3
1.43	7.2	50	3.65 ± 0.01	8 ± 1

TFE, as compared with the monotonic increase found for *t*-BuCl⁶ (Figure 1).

Solvolyses of 1-(*p*-methoxyphenyl)-2-methylpropenyl tosylate (4-OTs), brosylate (4-OBs), bromide (4-Br), and chloride (4-Cl) were followed conductometrically in the presence of 2,6-lutidine. For 4-OTs $10^4 k_1$ (35°) decreased steadily from 13.4 sec⁻¹ in 100% TFE to 7.13 sec⁻¹ in 50% TFE, $k_{4\text{-OBs}}/k_{4\text{-OTs}}$ ratios were 2.82 (100% TFE) and 3.14 (60% TFE), and the products were the corresponding ketone (5) and trifluoroethyl ether (4-OR).⁷

The solvolysis of 4-Br showed an extensive common ion rate depression within a run by the formed Br⁻. In 100% TFE, addition of 0.03 M Et₄NBr decreased k_1 11.5-fold, i.e., at least 92% of the products arise from "dissociated" vinyl cations.⁸ The "selectivity" values $\alpha = k_{\text{-ion}}/k_2$ were calculated according to eq 1



$$k_1^0 = k_{\text{ion}}/(1 + \alpha[\text{X}^-]) \quad (2)$$

and 2, and the k_1^0 values (= k_1 corrected for the external ion return) are given in Table I. A plot of k_1^0 values for 4-Br vs. $X_{\text{H}_2\text{O}}$ shows a minimum at ca. 90% TFE. The product distributions from 4-Br and 4-OTs were identical within the experimental error.⁹

External ion return is also shown by 4-Cl. The $k_{4\text{-Br}}/k_{4\text{-Cl}}$ ratio is 21 in 100% TFE.

The base-independent first-order kinetics for 1-OTs, 4-OTs, and 4-OBs, the adherence to eq 2 for both 4-Br and 4-Cl, the products, the $k_{\text{Br}}/k_{\text{Cl}}$, $k_{\text{OTs}}/k_{\text{Br}}$, and $k_{\text{OBs}}/k_{\text{OTs}}$ ratios, the lack of precedent for an in-plane nucleophilic vinylic substitution,¹⁰ and the S_N1 solvolysis of 4-OTs in AcOH-HCOOH¹¹ or CF₃COOH¹² rule out competing reactions such as electrophilic addition-elimination,¹³ nucleophilic addition-elimination,^{10,14} attack on sulfur,¹⁵ or an in-plane solvent assisted route k_s .¹⁶

(6) A plot of $\log k_1$ (1-OTs) vs. Y (*t*-BuCl) shows a similar minimum.

(7) The trifluoroethyl ether 4-OR is unstable in the presence of 2,6-lutidine and partially hydrolyzes to 5. It is more stable in the presence of Et₃N or NaOH.

(8) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Amer. Chem. Soc.*, **78**, 328 (1956).

(9) E.g., in 70% TFE the [4-OR]/[5] ratios are 35:65 from both 4-Br and 4-OTs in the presence of Et₃N.

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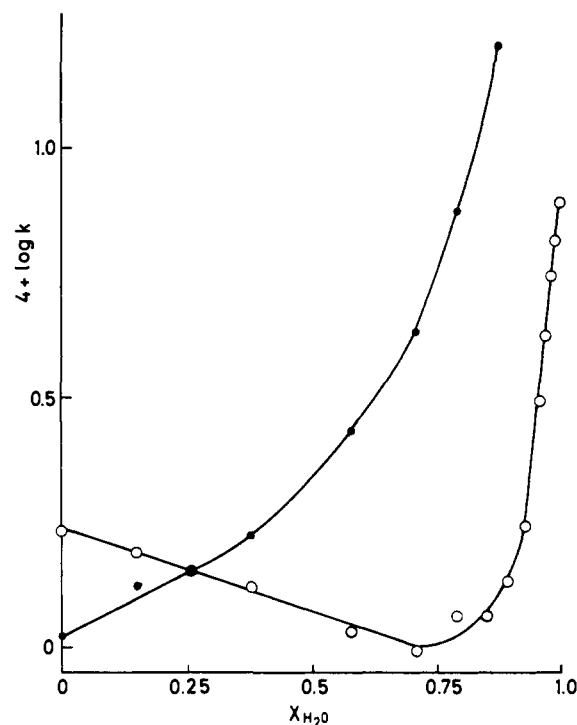


Figure 1. A plot of $\log k_1$ vs. $X_{\text{H}_2\text{O}}$ for 1-OTs at 35° (O) and for *t*-BuCl at 25° (●) in aqueous TFE.

The unusual behavior of the k_1 or k_1^0 values¹⁷ is connected with the special blend of solvent electrophilicity and dielectric constant of the media. Judging by the pK_a 's of water (15.75) and TFE (12.37),¹⁸ and by the conductivity data,¹⁹ anion (leaving group) solvation is enhanced in TFE compared with water while addition of water to TFE increases the dielectric constant.²⁰ The $\log k_1/X_{\text{H}_2\text{O}}$ dependency may result from the opposing effects of decreased electrophilic assistance and increased dielectric constant on k_{ion} (= k_1) with increasing $X_{\text{H}_2\text{O}}$. Alternatively, ion pairs may be involved and $k_1 = k_{\text{ion}}F$, where F is the fraction of ion pairs which lead to the product-forming dissociated ion, and k_{ion} decreases and F increases gradually on addition of water to the TFE.²¹

That a transition-state-like zwitterion is better solvated by TFE than by water is shown by the linear decrease of the energies ($E_T(1)$)²² of the internal charge transfer band of 1-(*p*-hydroxyphenyl)-2,4,6-triphenylpyridinium betaine²³ with $X_{\text{H}_2\text{O}}$ in the entire TFE-H₂O range.²⁴

An explanation in terms of TFE hydrates¹⁷ is ruled

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(17) D. E. Sunko and I. Szele, *Tetrahedron Lett.*, 3617 (1972), found a similar behavior in aqueous 1,1,1,3,3,3-hexafluoro-2-propanol.

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(21) The maximum observed in k_1^0 for *threo*-3-anisyl-2-butyl-OBs in AcOH-Ac₂O mixtures was explained in related terms: S. Winstein, R. Baker, and S. Smith, *J. Amer. Chem. Soc.*, **86**, 2072 (1964). This may be due to a difference in the shapes of the k_{ion} vs. $X_{\text{H}_2\text{O}}$ and F vs. $X_{\text{H}_2\text{O}}$ plots.

(22) The $E_T(1)$ values were measured in the presence of Et₃N.

(23) This is Dimroth's betaine 1: K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963).

(24) Our conclusion is based on the relationship between $E_T(30)$ and Y .²³

out by the absence of evidence for their formation²⁰ and the different positions of the minima for **1-OTs** and **4-Br**. The extent of ground-state solvation is not yet clear.

The decrease of α with X_{H_2O} has a precedent in the reaction of Ph_2CCl_2 in aqueous acetone.²⁵ A blend of effects (reduced recombination rate of R^+ with Br^- , enhanced cation solvation by water, reduced anion solvation by less TFE, change in the nucleophilicity of the medium, and possible intervention of ion pairs) account for this phenomenon.

A literature survey of solvolytic data in aqueous TFE reveals several peculiarities: (i) a minimum is also observable in Sunko's plot of $\log k_1$ vs. Y for MNBOTs;⁵ (ii) for cycloalkenyl triflates "m" (aqueous TFE) > "m" (aqueous EtOH), where "m" is based on two points²¹ (however, our data show that "high," "low," or "negative" m values may be obtained for different pairs of points, depending on the solvent mixtures chosen); (iii) "m" (aqueous TFE) for secondary brosylates are high,^{2b} probably reflecting a high response to the solvent nucleophilicity; (iv) the solvent isotope effect for the solvolysis of *t*-BuCl^{2a} and data on the addition of HCl to isobutene in TFE²⁶ suggest a rate determining dissociation of tight ion pairs in the trifluoroethanolysis.^{2a,26} Since the extent of the ion pair return is unknown, Y values of aqueous TFE are inadequate as a measure of the "ionizing power" and they should be used with reservation in mechanistic studies.^{27,28}

More work on solvolysis in aqueous TFE is now in progress.

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(27) For example, $Y(97\% \text{ TFE}) = 2.27$ when based on 1-adamantyl-Br,^{2b} 1.15 when based on *t*-BuCl,^{2a} and 0.79 when based on 4-OTs.

(28) E.g., the use of $k_{aq \text{ TFE}}/k_{aq \text{ EtOH}}Y$ for assessing the contribution of the k_s route (R. H. Summerville, C. A. Senkler, P. v. R. Schleyer, T. E. Dueber, and P. J. Stang, submitted for publication) may be highly misleading.

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Concerning Reported Nonnegligible Concentrations of Tetrahedral Intermediates in the Hydrolysis of Trifluoroacetanilides

Sir:

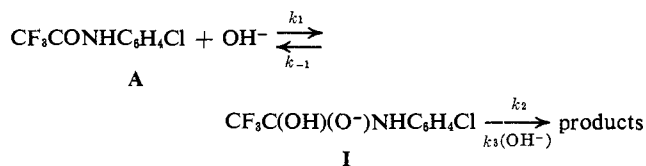
Tetrahedral species have long been postulated as intermediates in most reactions of carboxylic acid derivatives with nucleophiles.¹⁻³ More recently direct kinetic evidence for their intermediacy has been obtained in favorable cases,¹⁻⁹ and in a few cases such

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intermediates have been detected^{10,11} or even (for cyclic or polycyclic systems) isolated.¹²⁻¹⁴ Nevertheless it has been considered that such intermediates are ordinarily extremely unstable.^{1,15} Consequently a recent report of kinetic studies of the alkaline hydrolysis of substituted trifluoroacetanilides, in which it was stated that the tetrahedral intermediate accumulated to the extent of 5-10%,¹⁷ seemed quite startling. Furthermore the rate constants reported in this paper, from the kinetic analysis of the pH⁻¹ rate profile, correspond to an equilibrium constant of ca. 10^6 for the formation of I from A



Competitive ionization of the anilide ($pK_a = 9.2^{17}$) prevents complete conversion of A into I.¹⁸

We have performed an independent test for the accumulation of the species I. This took the form of an ¹⁹F nmr study of alkaline solutions of *p*-chlorotrifluoroacetanilide (A). In Table I are recorded ¹⁹F chemical shifts for trifluoromethyl groups in chemical environments similar to that of I. From the table it appears that replacing O by N causes a downfield shift of δ 1-3, with a smaller shift if the N bears an electronegative substituent, and replacing OH by O⁻ causes a δ 1.5 downfield shift. Then from the shifts for orthoesters of trifluoroacetic acid one estimates that the

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(15) This view is supported by recent work¹⁶ from this laboratory which led to evaluation of the free energy changes on addition of water to esters ($\Delta G^\circ = +12.1$ kcal/mol for methyl acetate).

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