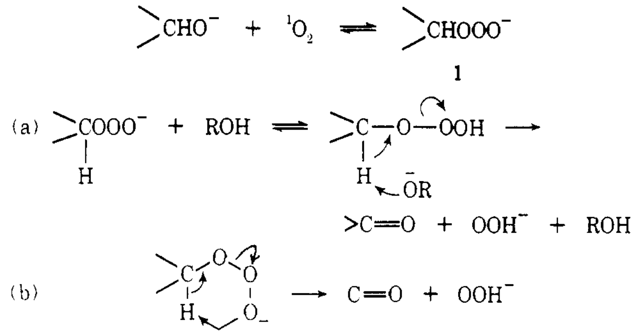
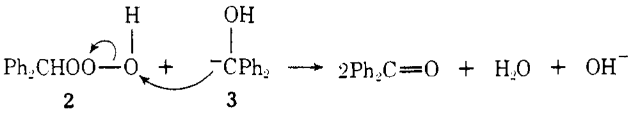
Scheme I



the mechanism outlined in Scheme I is a reasonable and attractive one for these reactions. In view of the fact that attempted photooxidations in aprotic solvents (DMF, pyridine, diglyme) proceeded with extreme sluggishness, if at all,[11] we favor the intermolecular process (a) for decomposition of the putative trioxide ion intermediate **1** rather than the intramolecular process (b). On the other hand, our results do not appear to rule out the possibility of mechanisms involving electron transfers.[12]

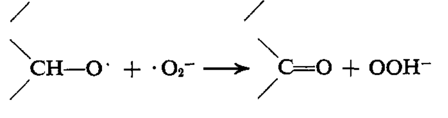
The photooxidation of benzhydrol in a solution of KOH in *tert*-butyl alcohol was unique among these studies in that complete conversion to benzophenone required only 0.5 mol of oxygen per mole of benzhydrol, and the resulting solution was free of peroxides. The possibility that half the benzhydrol was being oxidized by a rapid reaction with inorganic peroxide was ruled out by the fact that treatment of benzhydrol with a slight excess of hydrogen peroxide in a reaction mixture essentially identical with that used in the photooxidation produced at most a 2% yield of benzophenone. The contrast with the results from aliphatic alkoxides suggests that with benzhydrol there may be formed an appreciable concentration of the carbanion **3**, which could become hydroxylated[13] by reaction with a peroxidic intermediate such as **2**, formed during the photooxidation.



Acknowledgments. We thank the National Institutes of Health for financial support.

(11) Similar solvent effects have been noted in the oxidation of sulfides,[4] for which an intermediate analogous to **1** has been proposed.

(12) The following radical process is one such example



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Vinylic Cations from Solvolysis. XVII. An Unusual Solvent Effect and Common Ion Rate Depression in Aqueous Trifluoroethanol[1]

Sir:

2,2,2-Trifluoroethanol (TFE) and aqueous TFE mixtures have become popular solvolytic media.[2] This is due to the low nucleophilicity of TFE[2c,3] coupled with the relatively high "ionizing power" of the mixtures as judged by "Y" values[4] based on the solvolysis of *t*-BuCl ($Y_{\mathrm{TFE}} = 1.045$, $Y_{40\%\ \mathrm{TFE}} = 2.60$).[2a] Sunko, Szele, and Tomić found recently[5] that the solvolysis of 7-methyl-7-norbornyl tosylate (MNBOTs) in 100–70% TFE gave an m value of the Winstein–Grunwald equation,[4a] $\log (k/k_0) = mY$, of 0.062. They noticed that other secondary and tertiary systems gave much lower m values in aqueous TFE than in aqueous EtOH. These results prompt us to report the peculiar solvolytic behavior of several vinylic substrates in aqueous TFE.

Solvolysis of 1-(*o*-methoxyphenyl)-2-methylpropen-1-yl tosylate (**1-OTs**) was followed spectrophotometrically from 100% TFE to 2.5% (w/w) aqueous TFE (mole fraction of water $X_{\mathrm{H_2O}} = 0$–0.995) buffered with Et_3N. The products were the ether **1-OR** and the ketone **3**. From the product distribution, the relative rate ratios for capture of the intermediate carbonium ion **2** by water and TFE (in the presence of 2,6-lutidine) $k_{\mathrm{H_2O}}/k_{\mathrm{TFE}}$ are 0.83–1.20 in 97–80% TFE and they decrease in the more aqueous media. An unusual feature of the plot of $\log k_1$ *vs.* $X_{\mathrm{H_2O}}$ is the minimum at *ca.* 70%

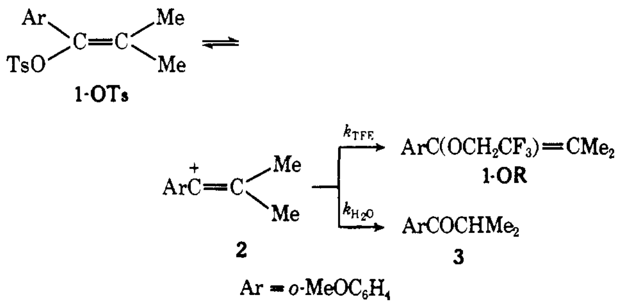

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Table I. $k_1°$ and α Values for the Solvolysis of **4-Br** at 35°

10^2[**4-Br**], mol l.$^{-1}$	10^2[2,6-Lutidine], mol l.$^{-1}$	% TFE (w/w) in TFE–H_2O	$10^5k_1^0$, 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*-BuCl[6] (Figure 1).

Solvolyses of 1-(*p*-methoxyphenyl)-2-methylpropen-1-yl 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** 10^4k_1 (35°) decreased steadily from 13.4 sec^{-1} in 100% TFE to 7.13 sec^{-1} in 50% TFE, $k_{\textbf{4-OBs}}/k_{\textbf{4-OTs}}$ 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* Et_4NBr 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

$$RX \underset{k_{-\text{ion}}}{\overset{k_{\text{ion}}}{\rightleftharpoons}} R^+ + X^- \xrightarrow[\text{SOH}]{k_2} ROS + H^+ \qquad (1)$$

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

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_{H_2O} 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 $k_{\textbf{4-Br}}/k_{\textbf{4-Cl}}$ 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_{Br}/k_{Cl}, k_{OTs}/k_{Br}, and k_{OBs}/k_{OTs} ratios, the lack of precedent for an in-plane nucleophilic vinylic substitution,[10] and the SN1 solvolysis of **4-OTs** in AcOH-HCOOH[11] or CF_3COOH[12] 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]

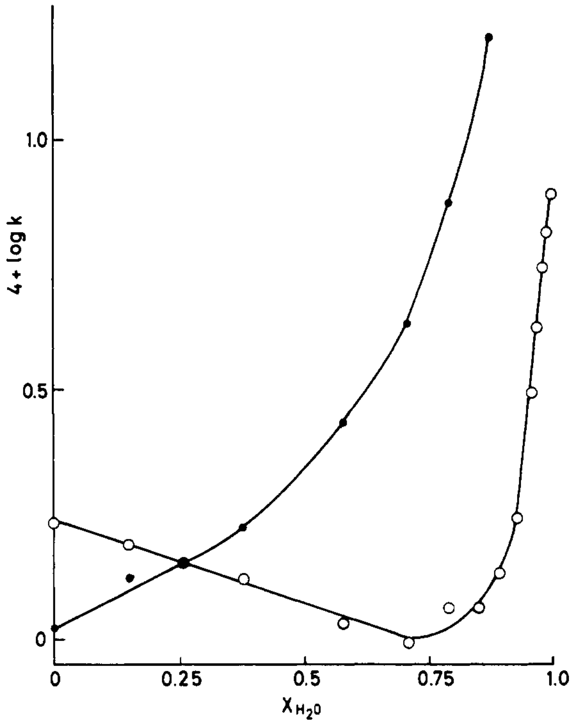

Figure 1. A plot of log k_1 *vs.* X_{H_2O} for **1-OTs** at 35° (○) and for *t*-BuCl at 25° (●) in aqueous TFE.

The unusual behavior of the k_1 or k_1^0 values[17] 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_{H_2O} dependency may result from the opposing effects of decreased electrophilic assistance and increased dielectric constant on k_{ion} ($=k_1$) with increasing X_{H_2O}. 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 betaine[23] with X_{H_2O} in the entire TFE–H_2O range.[24]

An explanation in terms of TFE hydrates[17] is ruled

(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 Et_3N 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 Et_3N.

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(22) The $E_T(1)$ values were measured in the presence of Et_3N.

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

out by the absence of evidence for their formation[20] 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 $X_{\mathrm{H_2O}}$ has a precedent in the reaction of $\mathrm{Ph_2CCl_2}$ in aqueous acetone.[25] A blend of effects (reduced recombination rate of $\mathrm{R^+}$ with $\mathrm{Br^-}$, 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 points[2i] (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 TFE[26] 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.

Acknowledgments. We are indebted to the Volkswagen Foundation for support of this work and to Professors E. M. Kosower and P. v. R. Schleyer for helpful discussions and preprints.

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[28] *E.g.*, the use of $(k_{\mathrm{aq\ TFE}}/k_{\mathrm{aq\ EtOH}})_Y$ 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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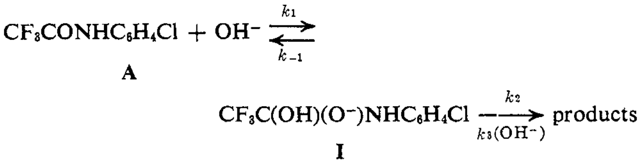
Concerning Reported Nonnegligible Concentrations of Tetrahedral Intermediates in the Hydrolysis of Trifluoroacetanilides

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 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 rate profile, correspond to an equilibrium constant of *ca.* 10^6 for the formation of I from A



$$\underset{\mathbf{A}}{\mathrm{CF_3CONHC_6H_4Cl}} + \mathrm{OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\mathbf{I}}{\mathrm{CF_3C(OH)(O^-)NHC_6H_4Cl}} \xrightarrow[k_3(\mathrm{OH^-})]{k_2} \text{products}$$

Competitive ionization of the anilide ($\mathrm{p}K_a = 9.2$[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 ^{19}F nmr study of alkaline solutions of p-chlorotrifluoroacetanilide (A). In Table I are recorded ^{19}F 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 $\mathrm{O^-}$ causes a δ 1.5 downfield shift. Then from the shifts for orthoesters of trifluoroacetic acid one estimates that the

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