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UNUSUAL REACTION CHEMISTRY IN THERMAL DECOMPOSITION OF ALKALI METAL 2-ALKOXY-2,3,3,3-TETRAFLUOROPROPIONATE SALTS

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SUMMARY

Pyrolyses of several salts $ROCF(CF_3)CO_2^-M^+$ (R=Me, Et, CF_3CH_2; M=Na, K, Cs) have been studied. The reaction chemistry shows highly unusual dependence on the nature of the alkoxy substituent and the metal cation. Product distributions are described along with some proposed mechanisms.

INTRODUCTION

Pyrolysis of alkali metal salts of perfluorinated carboxylic acids represents a useful synthetic route to unsaturated compounds such as perfluoroalkenes [1], perfluoro(alkylvinylethers) [2], and perfluoro(dialkylvinylamines) [3] (eqns. 1-3, R_f=perfluoroalkyl). These reactions can be carried out either with the dry salt or in a solvent such as tetraglyme. They may proceed via alkali fluoride elimination from carbanionic intermediates, as monohydrides are obtained in high yields [4] when a protic solvent such as ethylene glycol is used (eqn. 1b).

$$R_fCF_2CF_2CO_2^-M^+ \xrightarrow{\Delta} R_fCF{=}CF_2 + CO_2 + MF \qquad (1a)$$

$$\xrightarrow[SH]{} R_fCF_2CF_2H + CO_2 \qquad (1b)$$

$$R_fOCF(CF_3)CO_2^-M^+ \xrightarrow{\Delta} R_fOCF{=}CF_2 + CO_2 + MF \qquad (2)$$

$$(R_f)_2NCF(CF_3)CO_2^-M^+ \xrightarrow{\Delta} (R_f)_2NCF{=}CF_2 + CO_2 + MF \qquad (3)$$

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Little data exist with which to address the generality of the above decarboxylative eliminations--that is, how much can structural parameters such as fluorine content and distribution be varied before the reaction is diverted away from olefinic products? How sensitive is the reaction to the presence of hydrocarbon [5] substituents? In addition to their synthetic relevance, such questions may have interesting mechanistic ramifications. The large difference in the electronic nature of fluorine and hydrogen [6] may result in new intermediates and new product channels as the fluorine content is reduced from that of the perfluorinated systems in eqns. 1-3.

As part of an effort to begin probing the above issues, this report presents some observations relating to thermal decompositions of 2-alkoxy-2,3,3,3-tetrafluoropropionate salts 1. In addition to interesting and unexpected chemistry not seen in the

$ROCF(CF_3)CO_2^-M^+$

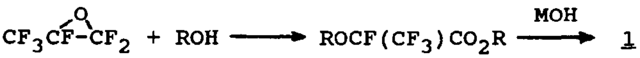
1

1a, $R=CH_3$, $M=Na$
1b, $R=CH_3$, $M=K$
1c, $R=CH_3$, $M=Cs$
1d, $R=C_2H_5$, $M=Na$
1e, $R=CH_2CF_3$, $M=Na$

perfluorinated analogues, the reactions exhibit some dramatic substituent and counterion effects. Product distributions are discussed along with some proposed mechanisms.

SYNTHESIS AND THERMAL DECOMPOSITION OF SALTS 1

The salts 1 were prepared by hydrolysis of esters 2 with alkali metal hydroxides; these were obtained [7] by addition of the appropriate alcohol to hexafluoropropylene oxide (eqn. 4).



$$CF_3\overset{O}{\overbrace{CF-CF_2}} + ROH \longrightarrow ROCF(CF_3)CO_2R \xrightarrow{MOH} 1 \qquad (4)$$

2

2a, $R=CH_3$
2d, $R=C_2H_5$
2e, $R=CH_2CF_3$

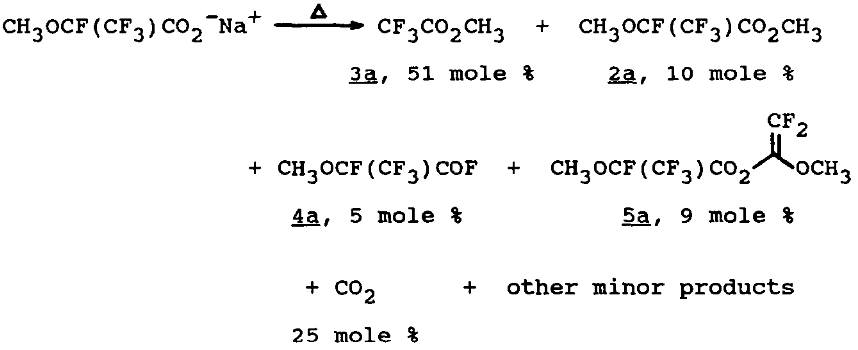
In the case of 2e, a solution of sodium trifluoroethoxide in trifluoroethanol was used, as reaction with the neutral alcohol was extremely sluggish.

Most of the salt pyrolyses were done on neat salts under vacuum at 220-300°C. Products were collected in a liquid nitrogen-cooled trap, then vacuum fractionated and subjected to GC/MS, IR, and NMR analysis (see Experimental.)

RESULTS

Decomposition of $CH_3OCF(CF_3)CO_2^-Na^+$ (1a)

Of the five salts examined in this work, 1a was the most extensively studied. At 225-300°C this salt was molten and decomposed smoothly to a nearly quantitative yield of sodium fluoride and the organic product mixture shown in (eqn. 5). Included in the



$$CH_3OCF(CF_3)CO_2^-Na^+ \xrightarrow{\Delta} \underset{\text{3a, 51 mole \%}}{CF_3CO_2CH_3} + \underset{\text{2a, 10 mole \%}}{CH_3OCF(CF_3)CO_2CH_3} + \underset{\text{4a, 5 mole \%}}{CH_3OCF(CF_3)COF} + \underset{\text{5a, 9 mole \%}}{CH_3OCF(CF_3)CO_2C(=CF_2)OCH_3} + \underset{\text{25 mole \%}}{CO_2} + \text{other minor products} \qquad (5)$$

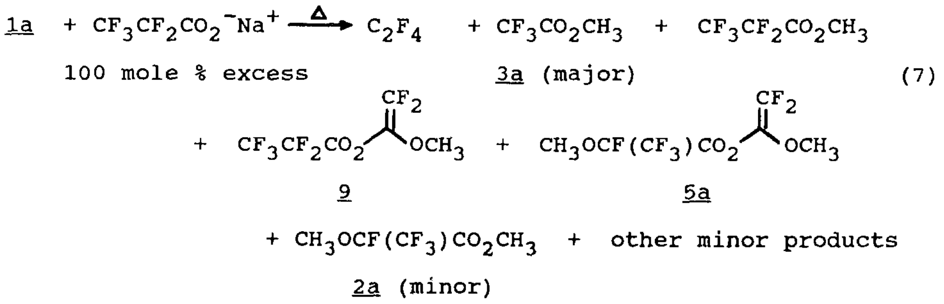
minor products were low levels of methyl trifluoropyruvate ($CF_3COCO_2CH_3$), methyl fluoride, and unidentified compounds. No methyl trifluorovinyl ether ($CH_3OCF{=}CF_2$) could be detected.

Sodium trifluoroacetate was observed in the solid residue as an intermediate when the reaction was interrupted. Also, CO was observed in the volatile products by infrared analysis but its yield was not quantified.

In hopes of trapping reactive intermediates, decomposition of 1a was examined qualitatively in the presence of other salts such as sodium benzoate and perfluoropropionate. Pyrolysis of a 2:1 molar mixture of sodium benzoate and 1a gave a complex organic product mixture containing the compounds shown in eqn. 6. Compound 5a was not observed when the reaction was run in the presence of sodium benzoate.

$$\underline{1a} + \underset{\substack{\text{100 mole \%}\\ \text{excess}}}{PhCO_2^-Na^+} \xrightarrow{\Delta} \underset{\underline{3a}\text{ (major)}}{CF_3CO_2CH_3} + \underset{\underline{6a}\text{ (minor)}}{CH_3OCF{=}CF_2} + \underset{\underline{7}}{CF_3COCO_2CH_3} + \underset{\underline{8a}}{PhCO_2CH_3} + \underset{\underline{8b}}{PhCOF} + \underset{\underline{2a}}{CH_3OCF(CF_3)CO_2CH_3} + \text{unknown products} \tag{6}$$

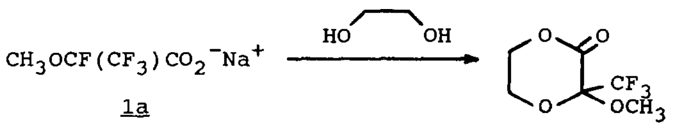
In the presence of excess sodium perfluoropropionate, decomposition of 1a gave the organic products shown in eqn. 7. In this case, note the low level of ester 2a.



$$\underline{1a} + \underset{\text{100 mole \% excess}}{CF_3CF_2CO_2^-Na^+} \xrightarrow{\Delta} C_2F_4 + \underset{\underline{3a}\text{ (major)}}{CF_3CO_2CH_3} + CF_3CF_2CO_2CH_3 + \underset{\underline{9}}{CF_3CF_2CO_2C({=}CF_2)OCH_3} + \underset{\underline{5a}}{CH_3OCF(CF_3)CO_2C({=}CF_2)OCH_3} + \underset{\underline{2a}\text{ (minor)}}{CH_3OCF(CF_3)CO_2CH_3} + \text{other minor products} \tag{7}$$

Compounds 5a and 9 are new compositions and were characterized by spectroscopic methods; samples of sufficient purity for elemental analysis could not be obtained. The presence of olefinic difluoromethylene in these compounds was confirmed by bromination and NMR analysis (see Experimental).

One final observation regarding decomposition of salt 1a is the formation of lactone 10 in low but unoptimized yield when the pyrolysis was run in ethylene glycol.



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Decomposition of $CH_3OCF(CF_3)CO_2^-M^+$ M=K (1b), Cs (1c)

Replacement of the sodium cation in 1a with potassium or cesium ions produced dramatic changes in the decomposition chemistry. In both cases methyl trifluorovinyl ether and methyl fluoride were observed (eqns. 8,9). These products seemed to be formed largely at the expense of 3a and 5a.

$$\begin{aligned} \underset{\underline{1b}}{CH_3OCF(CF_3)CO_2^-K^+} &\xrightarrow{\Delta} \underset{\underline{6a},\ 26\ \text{mole}\ \%}{CH_3OCF{=}CF_2} + \underset{\underline{2a},\ 12\ \text{mole}\ \%}{CH_3OCF(CF_3)CO_2CH_3} \\ &+ \underset{\underline{4a},\ 9\ \text{mole}\ \%}{CH_3OCF(CF_3)COF} + \underset{4\ \text{mole}\ \%}{CH_3F} + \underset{47\ \text{mole}\ \%}{CO_2} \\ &+ \underset{\underline{3a},\ 2\ \text{mole}\ \%}{CF_3CO_2CH_3} + \text{unidentified minor products} \end{aligned} \tag{8}$$

$$\begin{aligned} \underset{\underline{1c}}{CH_3OCF(CF_3)CO_2^-Cs^+} &\xrightarrow{\Delta} \underset{\underline{6a},\ 20\ \text{mole}\ \%}{CH_3OCF{=}CF_2} + \underset{19\ \text{mole}\ \%}{CH_3F} + \underset{50\ \text{mole}\ \%}{CO_2} \\ &+ \underset{\underline{4a},\ 6\ \text{mole}\ \%}{CH_3OCF(CF_3)COF} + \underset{\underline{2a},\ 2\ \text{mole}\ \%}{CH_3OCF(CF_3)CO_2CH_3} \\ &+ \underset{1\ \text{mole}\ \%}{(CF_3CO)_2O} + \underset{1\ \text{mole}\ \%}{CF_3COF} + \underset{1\ \text{mole}\ \%}{COF_2} \end{aligned} \tag{9}$$

Decomposition of $C_2H_5OCF(CF_3)CO_2^-Na^+$ (1d)

The decomposition products from pyrolysis of salt 1d formed a complex mixture which could not be completely characterized. However, the major components among the volatile products were ethylene and trifluoroacetaldehyde, CF_3CHO, formed in equimolar amounts, and lesser quantities of ethyl trifluoroacetate (3d), acetaldehyde, and ester 2d (eqn. 10). NMR analysis of the volatile products was aided by cold storage of the samples and obtaining the spectra at low temperatures. Very complex spectra resulted if the products were stored at room temperature before analysis; this is consistent with the known tendency of trifluoroacetaldehyde to polymerize [8].

$$\underset{\underline{1d}}{C_2H_5OCF(CF_3)CO_2^-Na^+} \xrightarrow{\Delta} C_2H_4 + CF_3CHO + \underset{\underline{3d}}{CF_3CO_2C_2H_5}$$

$$+ CH_3CHO + \underset{\underline{2d}}{C_2H_5OCF(CF_3)CO_2C_2H_5} + \text{other products} \qquad (10)$$

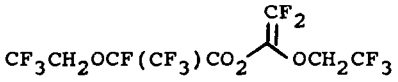
Decomposition of $CF_3CH_2OCF(CF_3)CO_2^-Na^+$ (1e)

Pyrolysis of salt 1e produced a mixture of products (eqn. 11, the major components of which were the trifluoroethyl analogues of the products from salt 1a (eqn. 5). However, the distribution was quite different, with 5e being a much more important product. Compound 5e was characterized in the same manner as 5a and 9.

$$\underset{\underline{1e}}{CF_3CH_2OCF(CF_3)CO_2^-Na^+} \xrightarrow{\Delta} \underset{\underline{3e},\ 20\text{ mole }\%}{CF_3CO_2CH_2CF_3} + \underset{\underline{6e},\ 4\text{ mole }\%}{CF_3CH_2OCF{=}CF_2}$$

$$+ \underset{\underline{4e},\ 6\text{ mole }\%}{CF_3CH_2OCF(CF_3)COF} + \underset{\underline{2e},\ 3\text{ mole }\%}{CF_3CH_2OCF(CF_3)CO_2CH_2CF_3}$$

$$+ \underset{38\text{ mole }\%}{CO_2} + \qquad (11)$$



$CF_3CH_2OCF(CF_3)CO_2C(=CF_2)OCH_2CF_3$

5e, 29 mole %

$$+ \text{unidentified minor products}$$

DISCUSSION -- PROPOSED MECHANISMS

Formation of $ROCF(CF_3)CO_2R$ and CH_3F--The Importance of Bimolecular Alkylation

The ester products 2 were found in the product mixtures from all salts studied. The most straightforward mechanism for their formation involves bimolecular alkylation of the starting salt. One possible alkylating agent is a second molecule of starting salt; another will be considered below. Several lines of reasoning support an S_N2-type origin for these products.

As shown in eqn. 12, bimolecular self-alkylation of the starting salt 1 would produce ester 2 and a second fragment which would likely degrade to metal fluoride, metal trifluoroacetate, and carbon monoxide. Thus, one mole of trifluoroacetate salt

$$2\ ROCF(CF_3)CO_2^-M^+ \longrightarrow \underset{\underline{2}}{ROCF(CF_3)CO_2R} + CF_3CF(O^-M^+)CO_2^-M^+ \qquad (12a)$$

$$CF_3CF(O^-M^+)CO_2^-M^+ \longrightarrow CF_3COCO_2^-M^+ + MF \qquad (12b)$$

$$CF_3COCO_2^-M^+ \longrightarrow CF_3CO_2^-M^+ + CO \qquad (12c)$$

would be produced for every mole of ester 2. Observation of trifluoroacetate as an intermediate product from 1a was discussed above, as was detection of carbon monoxide in the volatile products. Also, two substituent effects are consistent with an S_N2-type origin for ester 2. For R=CH_3, replacement of sodium with potassium produced an increase in the yield* of 2a, consistent with an increase in the nucleophilicity of the salt due to the more diffuse counterion [9]. Within the sodium salts, replacement of methyl with trifluoroethyl lowered the yield** of 2, as expected since S_N2 reactions on trifluoroethyl substrates are known [10] to be slower than on aliphatic analogues.

In the pyrolysis products from cesium salt 1c, little ester 2a was found; however, methyl fluoride, found only at trace levels from sodium salt 1a, was a major product. Upon progressing from sodium to cesium, the yield of methyl fluoride increased from near zero to 19 mole %, again in the order of increasing nucleophilicity of the metal fluorides. Thus, it seems likely that this product is formed by alkylation of fluoride ion rather than by elimination from the salts 1a-c. As was the case for ester 2 in eqn. 12, this mechanism (eqn. 13) requires equimolar production of methyl fluoride and trifluoroacetate salt.

$$F^-M^+ + CH_3OCF(CF_3)CO_2^-M^+ \longrightarrow CH_3F + CF_3CF(O^-M^+)CO_2^-M^+ \qquad (13a)$$

$$CF_3CF(O^-M^+)CO_2^-M^+ \longrightarrow CF_3CO_2^-M^+ + MF + CO \qquad (13b)$$

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* As a fraction of the organic products; note that the CO_2 yield is higher for the potassium salt 1b.

** Relative to the combined yields of 3 and 5 which, as discussed later, are believed to arise from a common intermediate.

Although methyl fluoride elimination from compounds such as ester 2a is a known process [11], this reaction requires strong acid catalysis, conditions which likely do not exist in these salt pyrolyses. Also, uncatalyzed unimolecular elimination is likely [12] to show a high activation energy and probably would not be important at the temperatures employed here.

One possible reason for the absence of ester 2a in the products from cesium salt 1c is that decarboxylation and fluoride loss to produce 6a is faster than bimolecular alkylation of the starting salt (eqn. 12a for M=Cs). This may be related to the absence of 6a in the products from sodium salt 1a, and is discussed in more detail in a later section.

The question remains as to the fate of the intermediate trifluoroacetate salt. As discussed in the next section, the evidence suggests that bimolecular alkylation of this intermediate is not the dominant mechanism for formation of the trifluoroacetate ester products. A more reasonable pathway for disappearance of trifluoroacetate may be formation of acid fluoride [13] as shown in eqn. 14. In support of this mechanism,

$$CF_3CO_2^- \longrightarrow CF_3^- + CO_2 \tag{14a}$$

$$CF_3^- \longrightarrow F^- + \ddot{C}F_2 \tag{14b}$$

$$\ddot{C}F_2 + ROCF(CF_3)CO_2^- \longrightarrow ROCF(CF_3)CO_2CF_2^- \tag{14c}$$

$$ROCF(CF_3)CO_2CF_2^- \longrightarrow \underset{\underline{4}}{ROCF(CF_3)COF} + CO + F^- \tag{14d}$$

note that in general the highest acid fluoride yields were found when bimolecular alkylation products (and hence production of trifluoroacetate salt) were most important, namely with the potassium and cesium salts 1b and 1c. However, although the yields of ester 2a and acid fluoride 4a were at least comparable from salt 1a, consistent with the stoichiometries expected for the mechanisms in eqns. 12 and 14, this was not the case for cesium salt 1c. The mechanisms proposed here do not account for why the acid fluoride yield from 1c was much less than that of methyl fluoride. Perhaps some other pathway exists for decomposition of the intermediate trifluoroacetate salt, or another mechanism is available for methyl fluoride formation. One formal possibility is unimolecular four-center elimination, although [12] it is difficult to conceive of this pathway being competitive with decarboxylation for 1c.

Finally, bimolecular formation of ester and acid fluoride products is confirmed by the observation that other carboxylates can participate. For instance, pyrolysis of a mixture of sodium benzoate and 1a gave methyl benzoate and benzoyl fluoride (8a-b), among other products (eqn. 6).

Formation of Alkyl Trifluoroacetates -- α-Lactone Intermediates?

Although yields varied depending on substituent and counterion, alkyl trifluoroacetates were observed in the pyrolysis products from all of the salts examined in this study save 1c. At least three mechanisms, shown in Fig. 1, can be written to account for their formation.

Scheme A in Fig. 1 involves alkylation of intermediate trifluoroacetate salt in a chain process. The experimental evidence tends against this mechanism; the substituent effect observed for salts 1a and 1e, in which replacement of methyl with trifluoroethyl has a larger effect on the yield of 2e than on that of 3e, suggests that the latter is not a product of an S_N2 reaction.

A second mechanism, shown in Scheme B of Fig. 1, is an intramolecular alkylation, loss of fluoride to give a trifluoropyruvate ester, and decarbonylation [14] to the trifluoroacetate. Like Scheme A, this mechanism involves a nucleophilic displacement reaction, and hence is not supported by experiment for the reasons discussed above. Methyl trifluoropyruvate was observed in the product mixture from salt 1a, but its yield was always quite low except when the pyrolysis was run in the presence of sodium benzoate, in which case it became a significant product. The dramatic effect of this added salt on the product distribution (eqn. 6) cannot be explained as yet. Although methyl trifluoropyruvate may be formed by the mechanism in scheme B, it is surprising that this product was not found in the products

Scheme A -- Alkylation of Intermediate Trifluoroacetate.

$$CF_3CO_2^- + ROCF(CF_3)CO_2^- \longrightarrow CF_3CO_2R + CF_3CF(O^-)CO_2^-$$

$$CF_3CF(O^-)CO_2^- \longrightarrow CF_3COCO_2^- + F^-$$

$$CF_3COCO_2^- \longrightarrow CF_3CO_2^- + CO$$

Scheme B -- Intramolecular S_N2 Alkylation.

$$ROCF(CF_3)CO_2^- \longrightarrow CF_3CF(O^-)CO_2R \longrightarrow CF_3COCO_2R + F^-$$

$$CF_3COCO_2R \longrightarrow CF_3CO_2R + CO$$

Scheme C -- Decarbonylation of α-Lactone.

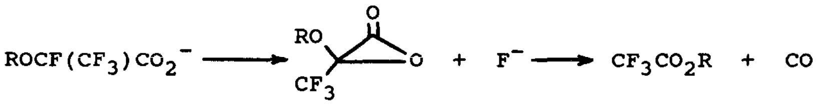

Fig. 1. Possible Mechanisms[a] for Formation of Alkyl Trifluoroacetates in Pyrolyses of Salts 1.

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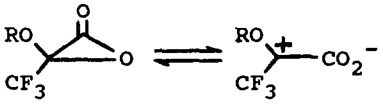
[a] The metal counterions have been omitted for clarity.

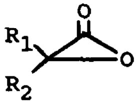
from the potassium and cesium salts 1b and 1c. Finally, formation of trifluoroacetate esters from trifluoropyruvates would require extremely rapid decarbonylation. This seems unlikely given that the latter are distillable compounds [11, 14] and their formation in these cases would occur under conditions (high temperature, low pressure) where distillation out of the reaction mixture would also be rapid.

Scheme C of Fig. 1 shows the mechanism for trifluoroacetate ester formation which appears most plausible in view of the available data. It involves loss of sodium fluoride as the first step, leading to an α-lactone 11 which could exist in either cyclic or open-chain zwitterion forms. CO loss from the cyclic form would product the corresponding trifluoroacetate ester.



11

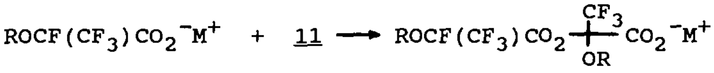
Good literature precedent exists for fluorinated α-lactones. Adam and co-workers [15] prepared the bis-trifluoromethyl α-lactone 12, while Coe and co-workers [16] have reported the perfluorinated α-lactone 13. Both products undergo facile decarbonylation to the respective perfluoroketones.



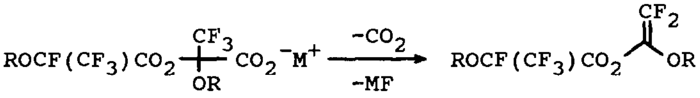
12, R_1, $R_2=CF_3$

13, $R_1=(C_2F_5)_2CCF_3$
$R_2=C_2F_5CFCF_3$

Compounds 5a, 5e, and 9 are proposed to arise from trapping of α-lactone intermediates by the appropriate salts (eqn. 15). That these products and the trifluoroacetate esters form via a common intermediate is suggested by the observation that their yields tracked each other. For instance, pyrolysis of 1a and 1e produced both types of products in significant yields, whereas in 1b and 1c the yields of 3a and 5a were both low.



$$\mathrm{ROCF(CF_3)CO_2^-M^+} \quad + \quad \underline{11} \longrightarrow \mathrm{ROCF(CF_3)CO_2}\overset{\mathrm{CF_3}}{\underset{\mathrm{OR}}{+}}\mathrm{CO_2^-M^+} \qquad (15a)$$



$$\mathrm{ROCF(CF_3)CO_2}\overset{\mathrm{CF_3}}{\underset{\mathrm{OR}}{+}}\mathrm{CO_2^-M^+} \xrightarrow[\mathrm{-MF}]{\mathrm{-CO_2}} \mathrm{ROCF(CF_3)CO_2}\overset{\mathrm{CF_2}}{\overset{\|}{\wedge}}\mathrm{OR} \qquad (15b)$$

5

Another possible reaction of an α-lactone intermediate with the starting salt leads to esters 2 via an alkyl transfer reaction (eqn. 16). Thus, in principle it is possible that α-lactone reactions account for formation of trifluoroacetate esters 3, esters 2, and trapping products 5 (and 9). However, for this to be the case, significant counterion effects on the branching ratios must be invoked to explain the relative yields. At this point it seems most likely that these products do not all arise from the same intermediate, but this cannot be demonstrated conclusively using available data.

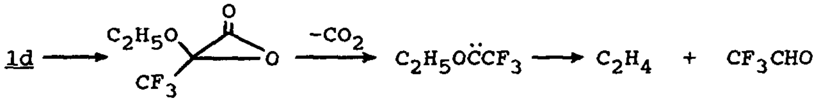
$$\underset{\underline{1}}{\mathrm{ROCF(CF_3)CO_2^-M^+}} \quad + \quad \underline{11} \longrightarrow \underset{\underline{2}}{\mathrm{ROCF(CF_3)CO_2R}} \qquad (16)$$

Evidence supporting an α-lactone intermediate in decomposition of salt 1a is provided by the isolation of lactone 10 when the reaction is run in ethylene glycol. This product can be regarded as the solvent trapping product of the proposed intermediate 11. None of the products of the dry salt pyrolysis are observed under these conditions.

Finally, before closing discussion of the α-lactone, one more possible reaction of this species deserves mention in that it involves a new type of organic intermediate. Decarboxylation of 11 would yield an alkoxytrifluoromethyl carbene (14, eqn. 17),

$$\underline{11} \longrightarrow \mathrm{CO_2} \quad + \quad \underset{\underline{14}}{\mathrm{RO\ddot{C}CF_3}} \longleftrightarrow \mathrm{R\overset{+}{O}{=}\overset{-}{C}CF_3} \qquad (17)$$

of which no examples exist in the literature. The push-pull nature of this carbene is illustrated by the ylid resonance structure shown in eqn. 17, and leads to a singlet ground state as predicted theoretically [17]. Reaction of salt 1 with 14 followed by metal fluoride elimination could lead to 5; also, intermediacy of a carbene is perhaps the most reasonable way to interpret formation of ethylene and trifluoroacetaldehyde in the decomposition of salt 1d, as shown in eqn. 18. Molecular orbital



(18)

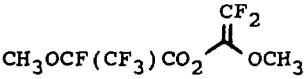
calculations planned for future work may help to assess the potential importance of the above reactions and intermediates in the salt decompositions discussed here.

Metal Fluoride Elimination vs. Decarboxylation -- Lattice Energy Effects

The remaining discussion may be couched in terms of comparisons between sodium salt 1a and cesium salt 1c (Table 1.) While 1a yielded methyl trifluoroacetate as the dominant organic product, 1c gave methyl trifluorovinyl ether and methyl fluoride. This dramatic counterion effect on product distribution can be rationalized by invoking metal fluoride lattice energy effects on the relative rates of the decarboxylation and fluoride elimination steps. Within the mechanistic scheme proposed here, the sodium salt undergoes elimination of sodium fluoride as the initial step, leading to α-lactone and products derived therefrom; the cesium salt decarboxylates first, leading to the 'normal' [2] trifluorovinyl ether product as in the perfluorinated analogues (eqn. 2). This divergent behavior implies an effect of the metal fluoride lattice energy on the rate of metal fluoride elimination, as the sodium fluoride lattice energy is larger than that of cesium fluoride [18]. Thus, in this mechanism the rate of metal fluoride elimination decreases on replacement of sodium with cesium in salt 1a. Alternatively, this substitution may

TABLE 1

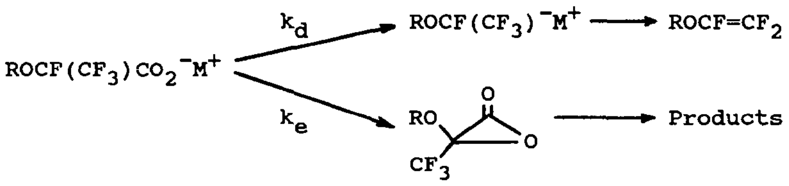
Distribution of Major Products from Pyrolysis of $CH_3OCF(CF_3)CO_2^-M^+$ (M=Na, K, Cs)

	Mole % yield[a]		
Product	M=Na	M=K	M=Cs
$CH_3OCF{=}CF_2$	ND	26	20
$CF_3CO_2CH_3$	51	2	ND
$CH_3OCF(CF_3)CO_2CH_3$	10	12	2
$CH_3OCF(CF_3)COF$	5	9	6
CH_3F	Tr	4	19
 $CH_3OCF(CF_3)CO_2C(=CF_2)OCH_3$	9	ND	ND

[a] ND=Not detected; Tr=Trace. The yields total less than 100% because of other products not listed in the table. See Results and Experimental sections.

increase the decarboxylation rate because the salt is less associated. Such behavior is observed in the pyrolyses of alkali metal trifluoroacetates [13a]. Kinetic studies are planned in hopes of distinguishing between these mechanistic alternatives.

Of course, the above counterion effect, whatever its origin, is superimposed upon an electronic effect of the aliphatic alkoxy group on the stability of the intermediate carbanion formed by decarboxylation (eqn. 19). As shown in eqn. 2, the perfluorinated analogues all yield vinyl ether regardless of counterion. Thus, for the perfluorinated salts, decarboxylation is faster than metal fluoride elimination. Replacement of the perfluoroalkoxy moiety with an aliphatic alkoxy destabilizes the intermediate carbanion (eqn. 19) and lowers the rate of decarboxylation such that metal fluoride loss can occur faster for those of higher



11

(19)

$k_d > k_e$ for R=perfluoroalkyl or M=Cs

$k_e > k_d$ for R=aliphatic and M=Na

lattice energies*. It is interesting to note the formation of low levels of trifluoroethyl trifluorovinyl ether in the products from sodium salt **1e**; evidently this substituent is sufficiently electron-withdrawing so as to induce some decarboxylation even from the sodium salt. Thus, within the sodium salts **1**, the progression from R=methoxy to trifluoroethoxy to perfluoroalkoxy results in an increase in vinyl ether yield from 0 (R=methoxy) to nearly quantitative (R=perfluoroalkoxy.) For the cesium salts, however, evidently metal fluoride elimination is always slower than decarboxylation independent of the nature of the alkoxy substituent, leading to vinyl ethers as the major products.

CONCLUSIONS

Pyrolysis of salts **1** reveals a wealth of interesting chemistry. The mechanistic scheme proposed herein interprets the observed products in terms of uni- and bimolecular reactions. The unimolecular reactions involve either decarboxylation or metal fluoride elimination as the key first steps, each pathway leading to its own unique set of products. Bimolecular reactions include alkylation of carboxylate and fluoride salts and trapping of proposed reactive intermediates such as alkoxytrifluoromethyl

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* Preliminary investigation of $CH_3OCF(CF_3)CO_2^-Li^+$ pyrolysis showed behavior similar to that of sodium salt **1a**, with methyl trifluoroacetate as the major product and no methyl trifluorovinyl ether observed. However, the product mixture also contained a complex array of higher-boiling products which were not characterized.

α-lactones and alkoxytrifluoromethyl carbenes. The relative importance of each type of reaction is dependent on counterion and alkoxy substituent. Metal fluoride lattice energies may play an important role in the reaction chemistry by governing the relative rates of decarboxylation and metal fluoride elimination.

Future work in this area will focus on several fronts. Molecular orbital calculations on intermediates should help to establish theoretical viability of the species and reactions discussed here. Isotopic labeling studies would be useful in determining the molecularity of mechanisms leading to products such as the alkyl trifluoroacetates. Finally, kinetics and effects of other substituents such as aryloxy or thioalkoxy remain completely unexplored and potentially useful tools for study of these intriguing reactions.

EXPERIMENTAL

NMR spectra were recorded with Varian XL-100 (^{19}F) or XL-400 (^{1}H, ^{13}C) instruments using $CFCl_3$, $CHCl_3$, or TMS as internal standards. Chemical shifts are reported in ppm upfield from $CFCl_3$ (^{19}F) or ppm downfield from TMS (^{1}H). Quantification of CO_2 was performed by integration of its ^{13}C signal at 128 recorded using a 20 kHz sweep width, 14.0 (90°) μsec pulse width, 0.75 sec acquisition time, and 200-250 sec recycle time.

Gas and liquid IR spectra were recorded using a Digilab Qualimatic FTIR. GC analyses were performed with a HP 5890 chromatograph equipped with a 10 m 530μ methylsilicone bonded-phase wide-bore capillary column and a thermal conductivity detector. GC/MS data were collected using a HP 5985 system for low-resolution spectra and a Nicolet FTMS-2000 for high-resolution measurements. In electron impact (EI) mode, ions were detected in the analyzer cell chamber at 2×10^{-7} torr; for self-chemical ionization (CI) measurements ions were detected in the source chamber at 1×10^{-6} torr. Perfluorotributylamine was added continuously to the source for mass calibration.

Preparation of Esters 2 and Salts 1

Esters 2a and 2d were prepared [7] by addition of hexafluoropropylene oxide (PCR) to methanol and ethanol. Ester 2e was prepared by bubbling hexafluoropropylene oxide into a refluxing solution of sodium trifluoroethoxide in trifluoroethanol. After the addition, the reaction mixture was poured into water and the lower layer was isolated, washed with water, dried, and distilled (bp 125-7°C, yield 39% based on trifluoroethoxide). High-resolution CI MS, m/e 327.0034 (P+1), calc. 327.0078 for $C_7H_4F_{10}O_3$ + H.

Salts 1 were prepared by hydrolysis of esters 2 with excess metal hydroxide, titration to pH 5-6 with aqueous HCl, evaporation to dryness, extraction with absolute ethanol (or acetone in the case of 1c,) filtration to remove insoluble metal chloride, and evaporation of solvent. The salts thus obtained showed no significant impurities by ^1H and ^{19}F NMR analysis.

Pyrolysis of $CH_3OCF(CF_3)CO_2^-Na^+$ (1a)

Salt 1a (1.34 g, 6.77 mmol) was dried by heating in a sand bath for 45 min at 150-190°C/0.01 torr. The remaining 1.33 g was pyrolyzed by raising the sand bath temperature to 300°C over the course of 90 min. Products were allowed to collect in a liquid nitrogen-cooled trap placed between the pyrolysis flask and the vacuum system. After a few min at 300°C, heat was removed. The residue showed a weight loss of 1.01 g (calculated, 1.05 g assuming NaF remaining), and the cold trap contained 0.90 g products.

The trap contents were fractionated under vacuum by warming the trap to room temperature and allowing volatile products to distill into an evacuated heavy-walled NMR tube cooled in liquid nitrogen. The tube had been spiked with drops of $CFCl_3$ and $CHCl_3$ before the distillation. A total of 0.64 g products collected in the tube, which was then sealed. The remaining 0.26 g products in the trap was vacuum transferred into a liquid nitrogen-cooled finger by gentle warming. This gave 0.23 g liquid transferred and left 0.03 g residue (discarded) in the trap.

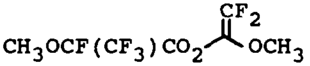
NMR analysis of the sealed tube sample, and NMR and GC analysis of the higher-boiling fraction showed that the products consisted of 0.81 g with the molar composition shown in eqn. 5, and 0.09 unknown material.

Spectroscopic Data

$CF_3CO_2CH_3$ - ^{1}H NMR - δ3.87 (s); ^{19}F NMR - δ75.5 (s).

$CH_3OCF(CF_3)COF$ - ^{1}H NMR - δ3.6 (s); ^{19}F NMR - δ81.5 (3F, dd, J=3, 6 Hz), δ132.6 (1F, m), δ-28.8 (1F, q, J=6 Hz).

$CH_3OCF(CF_3)CO_2CH_3$ - ^{1}H NMR - δ3.48 (s), δ3.82 (s); ^{19}F NMR - δ81.6 (3F, d, J=3 Hz), δ134.9 (1F, m).



$CH_3OCF(CF_3)CO_2C(=CF_2)OCH_3$ - ^{1}H NMR - δ3.65 (s), δ3.79 (s); ^{19}F NMR δ81.3 (3F, d, J=3 Hz), δ134.2 (1F, m), δ114.5 and 116.3 (2F, AB, J=80 Hz). IR - $\nu_{C=O}$ = 1810 cm^{-1}, $\nu_{C=C}$ = 1765 cm^{-1} [19]. CI MS - m/e 269.0361 (P+1), calc. 269.0248 for $C_7H_6F_6O_4$ + H.

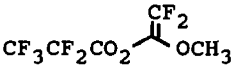
Pyrolysis of 1a with Excess Sodium Benzoate

A mixture of 0.98 g (4.9 mmol) 1a and 1.42 g (9.9 mmol) sodium benzoate was ground to a fine powder, then pyrolyzed at 230°C/0.01 torr for 105 min, collecting the products in a liquid nitrogen-cooled trap. The pyrolysis residue showed a weight loss of 0.52 g. Vacuum fractionation of the products and analysis by NMR and GC indicated the presence (yields >10%) of the compounds shown in eqn. 6. One significant product, displaying a GC retention time longer than those of the other products in eqn. 6, was not identified but contained no fluorine by GC/MS.

Pyrolysis of 1a with Excess Sodium Perfluoropropionate

A mixture of 0.99 g (5 mmol) 1a and 1.86 g (10 mmol) sodium perfluoropropionate was ground to a fine powder and pyrolyzed at 205°C/0.01 torr for 25 min, collecting the products in a liquid nitrogen-cooled trap. The sample showed a weight loss of 0.91 g. CO_2 and C_2F_4 were allowed to distill out of the product mixture, then the remaining 0.79 g products were vacuum fractionated and analyzed by NMR and GC. Products formed in yields >10% of the product mixture are shown in eqn. 7. Among the minor products were ester 2a and acid fluoride 4a.

Spectroscopic Data



$CF_3CF_2CO_2C(=CF_2)OCH_3$ - ^{1}H NMR - δ3.80 (s); ^{19}F NMR - δ83.1 (3F, t, J=2 Hz), δ121.4 (2F, q, J=2 Hz), δ113.4, 115.5 (2F, AB, J=78 Hz). EI MS - m/e 255.9973 (P), calc. 255.9970 for $C_6H_3F_7O_3$.

Pyrolysis of 1a in Ethylene Glycol

Salt 1a (2.0 g, 10.1 mmol) was placed in 10 g ethylene glycol. This mixture was stirred and heated at 200°C for 1 hr under nitrogen. No volatile products were obtained. The reaction mixture was cooled, pressure-filtered through glass wool, and the filtrate extracted with excess $CFCl_3$. Isolation and evaporation of the $CFCl_3$ left 0.27 g (13% yield) lactone 10. Analysis of the ethylene glycol layer by ^{19}F NMR showed two singlets in the trifluoroacetyl region (δ75).

Spectroscopic Data for 10 - ^1H NMR - δ4.12, 4.50 (4H, m), δ3.47 (3H, s); ^{19}F NMR - δ78.2 (s). IR - $\nu_{C=O}$ = 1768 cm^{-1}. CI MS - m/e 201.0460 (P+1), calc. 201.0374 for $C_6H_7F_3O_4$ + H.

Pyrolysis of Salt 1b

In a manner identical to that described above for 1a, 0.75 g (3.5 mmol) salt 1b was dried at 160°C/0.01 torr for 30 min, then pyrolyzed by raising the sand bath temperature to 250°C. After cooling, the flask residue showed a weight loss of 0.45 g (calculated, 0.53 g assuming KF). Some of the salt had sublimed out of the hot zone during reaction, preventing complete decomposition. Products were vacuum fractionated as described above to give 0.32 g volatiles which were sealed in a heavy-walled NMR tube, 0.11 g higher-boiling liquid fraction, and 0.02 g solid residue (discarded). Analysis of the sealed tube fraction by NMR, and analysis of the higher-boiling liquid fraction by GC and NMR showed that the products consisted of 0.42 g with the composition shown in eqn. 8, and 0.03 g unknown material.

Spectroscopic Data

$CH_3OCF=CF_2$ [23] - ^1H NMR - δ3.75 (s); ^{19}F NMR - δ125.4 (1F, dd, J=56, 108 Hz), δ132.0 (1F, t, J=108 Hz), δ138.3 (1F, dd, J=56, 108 Hz).

CH_3F - ^1H NMR - δ4.18 (d, J=46 Hz); ^{19}F NMR - δ270.6 (q, J=46 Hz).

Pyrolysis of Salt 1c

In a manner identical to that described above for 1a, 1.08 g (3.5 mmol) salt 1c was dried by heating to 160°C/0.01 torr (salt melted ~80°C), inducing a weight loss of 0.02 g. The remaining 1.06 g was pyrolyzed by raising the bath temperature to 200°C, then to 290°C over 30 min. After 30 min at 290°C, heat was removed. The pyrolysis residue showed a weight loss of 0.51 g (calculated, 0.54 g assuming CsF). Products were vacuum fractionated as described above to give 0.41 g volatiles, 0.03 g higher-boiling liquid fraction, and 0.02 g liquid residue (discarded). Analysis of the product fractions as described above for 1a and 1b showed the 0.46 g products to consist of 0.43 g with the composition shown in eqn. 9, and 0.03 g unknown material

Spectroscopic Data

CF_3COF - ^{19}F NMR - δ-14.9 (1F, q, J=7 Hz), δ74.9 (3F, d, J=7 Hz).

COF_2 - ^{19}F NMR - δ22.9 (s).

$(CF_3CO)_2O$ - ^{19}F NMR - δ75.6 (s).

Pyrolysis of Salt 1d

In a manner identical to that described above for 1a, 1.22 g (5.75 mmol) salt 1d was dried for 1 hr at 120-170°C/0.01 torr. This induced a weight loss of 0.03 g. The remaining 1.19 g was pyrolyzed at 225-260°C for 40 min. The residue showed a weight loss of 0.94 g (calculated, 0.95 g assuming NaF). Products were vacuum fractionated as described above to give 0.60 g volatiles, 0.26 g higher-boiling liquid fraction, and 0.06 g residue (discarded). After storage in liquid nitrogen, NMR analysis of the sealed tube sample showed the primary organic components to be an equimolar mixture of ethylene (^1H NMR - δ5.30 (s)) and trifluoroacetaldehyde (^1H NMR - δ9.27 (q, J=3 Hz); ^{19}F NMR - δ82.3 (d, J=3 Hz). Ethyl trifluoroacetate was also present, albeit in lower yield. Acetaldehyde and several unidentified compounds were observed as very minor products. The higher-boiling fraction was found by GC to contain at least 6 different components, including ester 2d.

Pyrolysis of Salt 1e

In a manner identical to that described above for 1a, 1.01 g (3.8 mmol) salt 1e was dried at 120-160°C/0.01 torr for 1 hr, then pyrolyzed at 200-300°C/0.01 torr for 45 min. The pyrolysis residue showed a weight loss of 0.77 g (calculated, 0.85 g assuming NaF). Products were vacuum fractionated as described above to give 0.25 g volatiles, 0.41 g higher-boiling liquid fraction, and 0.02 g residue (discarded). Analysis of the product fractions as described above showed that the products consisted of 0.64 g with the molar composition shown in eqn. 11, and 0.04 g unknown material.

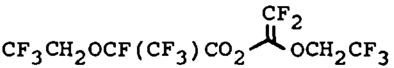
Spectroscopic Data

$CF_3CO_2CH_2CF_3$ - ^{1}H NMR - δ4.67 (q, J=8 Hz); ^{19}F NMR - δ75.1 (3F, s), δ74.6 (3F, t, J=8Hz).

$CF_3CH_2OCF(CF_3)COF$ - ^{19}F NMR - δ-27.5 (qn, J=6 Hz), δ81.0 (3F, dd, J=4, 6 Hz), δ131.7 (1F, m), δ75.1 (3F, t).

$CF_3CH_2OCF{=}CF_2$ [20] - ^{19}F NMR - δ75.4 (3F, tm, J=7 Hz), δ122.0 (1F, dd, J=60, 102 Hz), δ127.9 (1F, tm, J=103, 2 Hz), δ138.3 (1F, ddm, J=60, 108, 2 Hz).

$CF_3CH_2OCF(CF_3)CO_2CH_2CF_3$ - ^{19}F NMR - δ74.6 (3F, t, J=8 Hz), δ75.2 (3F, td, J=8, 2 Hz), δ81.4 (3F, d, J=4 Hz), δ132.9 (1F, m).



$CF_3CH_2OCF(CF_3)CO_2C(=CF_2)OCH_2CF_3$ - ^{1}H NMR - δ4.18 (q, J=8 Hz), δ4.24 (q, J=8 Hz); ^{19}F NMR - δ75.2 (3F, td, J=8, 2 Hz), δ75.6 (3F, td, J= 8, 2 Hz), δ81.2 (3F, d, J=4 Hz), δ132.7 (1F, m), δ111.2, 112.3 (2F, AB, J=72 Hz; high-field branches of AB pattern are further split into J=2 Hz quartets). CI MS - m/e 405.0053 (P+1), calc. 404.9995 for $C_9H_4F_{12}O_4$ + H.

Reaction of 5a with Bromine

A product fraction from 1a pyrolysis which was 65 mole % 3a, 17 mole % 2a, 12 mole % 5a, and 6 mole % 4a by ^{19}F NMR was dissolved in $CFCl_3$ and treated with bromine until the color persisted. This caused a slight warming of the sample. After a few minutes, the ^{19}F NMR spectrum was scanned again. The major changes were replacement of the 5a AB quartet with a new AB pattern (further split into doublets) with branches centered at δ56.8 and 60.5 (J_{AB}=164 Hz), and splitting of the δ81.5 and 132.6 signals of 5a into doublets*. All signals for 3a, 2a and 4a were unchanged. A minor peak at δ61.3 which appeared upon bromination may be due to methyl bromodifluoroacetate arising from decomposition of the 5a bromination product.

Samples containing 5e and 9 behaved similarly upon treatment with bromine.

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