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Heterolytic decarboxylation involving acyltrifluoroacetyl peroxide intermediates

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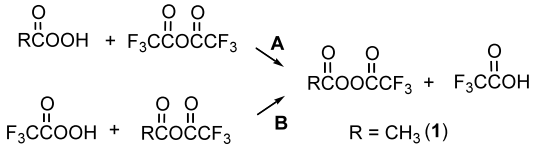
Abstract—Selective carboxylic acid decarboxylation was elaborated. Generation of acyltrifluoroacetyl peroxides from carboxylic peracids and trifluoroacetyl anhydride (Method A), as well as from trifluoroperacetic acid and acyltrifluoroacetyl anhydride (Method B), leads to simultaneous peroxide decomposition into the corresponding alkyltrifluoroacetates. DFT computations, as well as experimental data, support an acid-catalyzed heterolytic mechanism for acyltrifluoroacetyl peroxide decomposition.

Our previous communication describing the catalytic method for bis(perfluoroacyl)peroxides synthesis[1] included an attempt at acetyltrifluoroacetyl peroxide synthesis. It was shown that acetyltrifluoroacetyl peroxide[1,2] can be prepared in situ (Scheme 1) from the corresponding peracetic acid and trifluoroacetyl anhydride (Method A), or from trifluoroperacetic acid and acetyltrifluoroacetyl anhydride (Method B).

The remarkably low stability of acyltrifluoroacetyl peroxides prompted us to develop a method for carboxylic acid decarboxylation involving acyltrifluoroacetyl intermediates. To achieve this goal, a variety of carboxylic acids (**2**–**13**, Table 1) were used to generate acyltrifluoroacetyl peroxides in TFAA (Scheme 1). Method **A** assumes the preparation of the corresponding peroxy acids as starting materials.[3,4] Decarboxylation by Method B occurs by adding a solution of trifluoroperacetic acid (TFPAA) in trifluoroacetic acid (TFAA) into a solution of carboxylic acid in trifluoroacetic anhydride (TFAAn).[5] In both cases, mixing of the reagents coincides with an immediate decarboxylation above −20°C and the formation of alkyl trifluoroacetates (**16**–**24**, 92–99% yields, Table 1). GC/MS analysis of the reaction mixtures indicated the formation of small amounts of by-products. In most cases trifluoroacetates were separated and their structures were in good agreement with an independently synthesized.[6,7] The yield and product distribution for acids **3**–**5** were verified by ^{1}H NMR analysis using 1,4-ditrifluoromethylbenzene as internal standard. The structure and distribution of compounds **21**/**19** were confirmed by ^{1}H NMR analysis, while distribution of compounds **22/23** were shown by GC/MS analysis and by comparison with independently-synthesized trifluoroacetates **19**, **21**, **22** and **23**.[6] Methods A and B provided essentially no difference in reaction product distribution (±5%).[7] The yields of the corresponding trifluoroacetates obtained by Method A usually were higher than by Method B. However, the presence of carboxylic acid in the starting peroxy acid (Method A) may decrease the yield of decarboxylation because of the formation of the corresponding stable diacylperoxides. In contrast to acids **5**–**13**, the reactions of acids **2**–**4** yielded the corresponding intermediate acyltrifluoroacetyl peroxides **1**, **14** and **15**, which are relatively stable at 0°C (**1**, **14**) and −40°C (**15**) (Table 1). The acetyltrifluoroacetyl peroxide **1** is stable at room temperature, while peroxides **14** and



Scheme 1.

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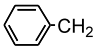
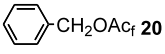
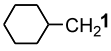
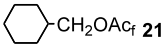
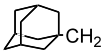
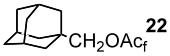
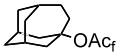
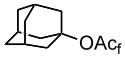
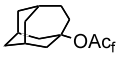
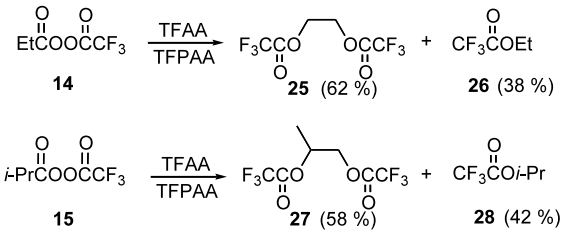
Table 1. RCOOH decarboxylation in TFAA

Entry	RCOOH R=		Products		yield (%)
1	Me	**2**	$MeCOOOAc_f$	**1**	100
2	Et	**3**	$EtCOOOAc_f$	**14**[a]	100[d]
3	*i*-Pr	**4**	*i*-$PrCOOOAc_f$	**15**[b]	100[d]
4	*t*-Bu	**5**	t-Bu-OAc_f	**16**	95
5		**6**		**17**	93
6		**7**		**18**	96
7		**8**		**19**	92
8		**9**		**20**	99
9		**10**		**21**	54
				**19**	39
10		**11**		**22**	5
				**23**	91
11		**12**[c]		**24**	98
12		**13**[c]		**23**	97

Ac_f=CF_3CO. [a] Synthesized at 0 °C. [b] Synthesized at -40 °C. [c]Decarboxylation only by method **B.** [d] For the distribution of decarboxylation products see Scheme 2.

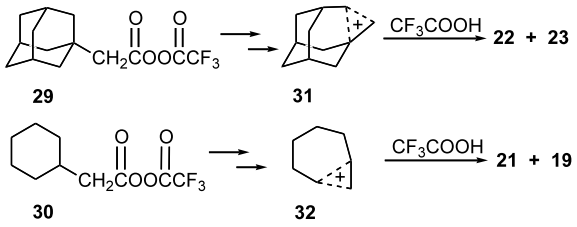


Scheme 2.

15 undergo decarboxylation into a mixture of trifluoroacetates **25**–**28** (Scheme 2).

The thermal decomposition of bis(perfluoroacyl) peroxides has been studied previously[9] and was found useful for the initiation of radical polymerization[10] and radical perfluoroalkylation processes.[11] Thermal decomposition leads to perfluoroalkanes (R_f–R_f) via radical recombination.[9] Table 1 and Scheme 2 display an entirely different set of products formed in the TFAA. These results suggest a non-radical mechanism for peroxide decomposition.[12]

Thus, the formation of ditrifluoroacetate by-products **25**, **27** suggested subsequent olefinization, epoxidation,



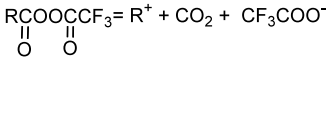
Scheme 3.

and oxirane ring opening of carbocationic intermediates (Et^+ and *i*-Pr^+).[13] Trifluoroacetates **26** and **28** were stable under the decarboxylation conditions and, therefore, can be excluded as possible intermediates in such transformations.

The observed ring expansion of acids **10** and **11** (Table 1) also approved a heterolytic mechanism for peroxides **29** and **30** decomposition (Scheme 3) through cations **31** and **32**.[14–17]

Trifluroroacetates **19** and **23** may also be formed from trifluoroacetates **21** and **22** through a solvolytic mechanism. However, the stability of trifluoroacetates **21** and **22** in TFAA (even upon heating) suggested the intermediate formation the 3-homoadamantyl (**31**) and cycloheptyl (**32**) cations (Scheme 3) generated during peroxide **29**, **30** decomposition. The ratios **23**:**22** = 91:5,[14,15] and **19**:**21** = 39:54, typically correspond to a kinetically-controlled reaction,[15] which would proceed through carbocationic intermediates.[14–17] The polarity, the acidity and the nucleophilicity of the reaction media may also slightly influence this ratio. It is important to note that the observed reaction selectivity and ring expansion reactions are consistent with adamantane/homoadamantane,[15,16] and cyclohexane/cycloheptane[18] cationic chemistry, and inconsistent with radical transformations.

In order to estimate the thermodynamic feasibility of heterolytic (Eq. (1)) decomposition of acetyl-, propionyl-, methylpropionyl-, and pivaloyltrifluoroacetyl peroxides, DFT computations utilizing a B3LYP method with 6-31G(d) basis set, as implemented in a Gaussian 98 program package were carried out.[19] Computations indicate that heterolytic decomposition from a neutral intermediate is very unfavorable. However, under the polar and acidic conditions which were used for decarboxylation,[7] the protonated forms of the acyltrifluoroacetyl peroxides appeared to be more appropriate starting species for heterolytic decomposition (Eq. (2)). In contrast to the thermodynamically unfavorable heterolytic decomposition of the non-protonated forms (Eq. (1)), highly exothermic decomposition of the protonated species (Eq. (2)) supported an acid-catalyzed mechanism.



R	Δ*E*, kcal/mol
Me	163.3
Et	122.8
i-Pr	92.3
t-Bu	82.8

(1)

$$RCOOCCF_3 = R^+ + CO_2 + CF_3COOH \quad (2)$$

R	ΔE, kcal/mol
Me	0.8
Et	-38.5
i-Pr	-63.5
t-Bu	-77.5

Previously proposed mechanisms for ionic decomposition of unsymmetrical peroxides were based on the observation of carbonates formed in the carboxy-inversion process.[12] With the current method, we encounter the optimum conditions for an ionic process, including the internal polarization of an acyltrifluoroacetyl molecule in polar and acidic reaction media.

The combination of these factors leads to the possibility of a different mechanistic scenario and prompted the computational modeling of the reaction mechanism for the protonated forms of the acyltrifluoroacetyl peroxides. The calculation results are presented in Fig. 1 (relative energies in kcal mol^{-1}).

The transition structures (**TS1**–**TS4**, Figs. 1 and 2) were located on the reaction pathway to the carbocationic $[R\cdots OCO]^+$ complexes through the loss of TFAA. Decarboxylation occurs concertedly (IRC) during the cleavage of the R–C and CO–OC bonds and the formation of a new R–OCO bond. The substantial differences in the critical R–O and O–O distances from 2.196 and 1.878 Å in the *late* **TS1** to 2.355 and 1.634 Å in *early* **TS4** are in the agreement with the computed reactions exothermicities (Fig. 1). Resulting $[R–OCO]^+$ clusters are either more (R = Me and R = Et) or less (R = *i*-Pr and R = *t*-Bu) bounded. There is almost no bonding between R^+ and CO_2 in the $[i\text{-Pr–OCO}]^+$ and $[t\text{-Bu–OCO}]^+$ clusters as the $R^+\cdots OCO$ distances are rather high (2.710 and 2.922 Å) and the net charges on hydrocarbon parts are close to +1e. The dissociation energies of these complexes are negligible (Fig. 1). Thus, solvated carbocations could be formed directly as a result of heterolytic decarboxylation of protonated $RC(O)OOC(O)CF_3$ (R = *i*-Pr and *t*-Bu) in the TFAA media. Relatively low barriers were found for all reactions; the decrease of the barrier in the order **TS1**>**TS2**>**TS3**>**TS4** (Fig. 1) reflects an R^+ stability. The barrier for fragmentation of protonated peroxide **1** is relatively high (10.0 kcal mol^{-1}), and this explains the relative stability of **1** in the TFAA/TFAAn media (vide supra). However, a more detailed evaluation of this mechanism is in progress.

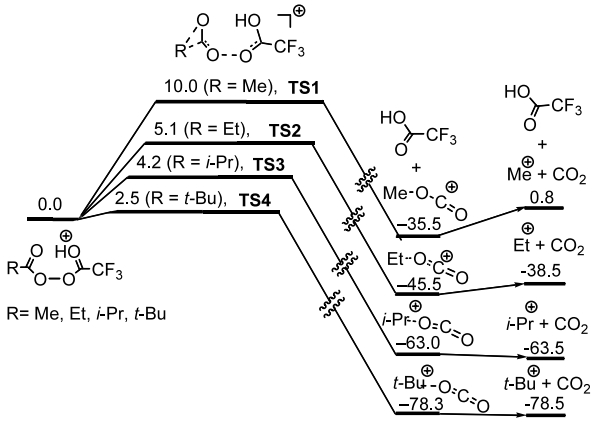


Figure 1. The B3LYP/6-31G* (**TS1**–**TS4**) barriers and reaction energies (kcal/mol) for the decarboxylation of protonated peroxy anhydrides.

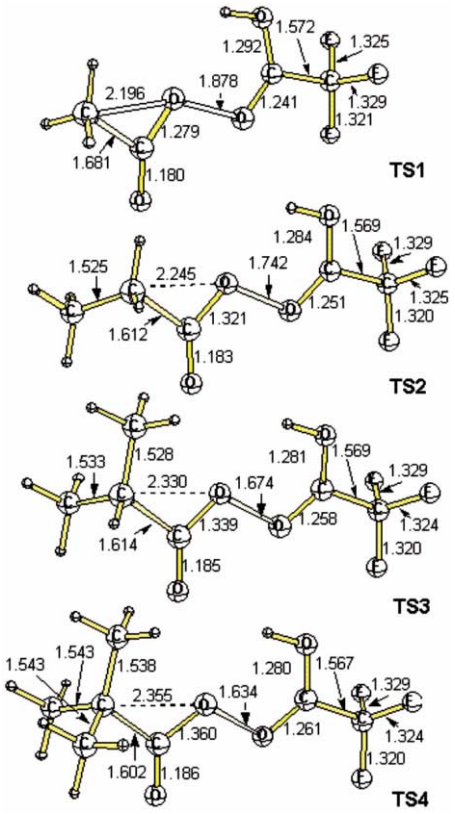


Figure 2. The B3LYP/6-31G* optimized geometries (bond distances in Å) of the transition structures **TS1**–**TS4**.

Acknowledgements

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4. **Perpropionic acid and 2-methylperpropionic acid** were prepared by a modified literature procedure[3b] from propionic acid (**3**) and 2-methylpropionic acid (**4**), respectively: H_2O_2 (35% solution in water, 110 g) was added dropwise into a well-stirred solution of carboxylic acid (0.1 mol), H_2O (30 ml), and H_2SO_4 (35 g, 0.36 mol) at 0°C and stirred for 1 h. The reaction mixture was then extracted with CCl_2FCF_2Cl (12×10 ml). The combined organic extracts were treated with a buffer solution (pH 8.0) until all carboxylic acid was removed and then dried over Na_2SO_4. Half of the solvent was evaporated at 20°C and quality of the solution of peracid in CCl_2FCF_2Cl was confirmed by ^1H NMR and by iodometric titration and used without further purification.
5. Trifluoroacetic anhydride (TFAAn) must be a freshly distilled and stored in a Teflon® bottle. A solution of TFPAA in TFAA must be prepared from freshly distillated TFAAn and stored in a Teflon® bottle. For more information, see Ref. 1
6. **Preparation of trifluoroacetates 16–28**: Trifluoroacetates were prepared by adding the corresponding alcohol (1 mmol) into trifluoroacetic anhydride (3 ml) at 0°C and stirring for 0.5 h. The solvent was then evaporated and trifluroacetates **17–25** were obtained in a quantitative yield. **1-Adamantylmethyl trifluoroacetate (22)**: IR (film, cm^{-1}): 2965–2840, 1778, 1185. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.94 (s, 2H), 2.02 (m, 3H), 1.8–1.5 (m, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 155.8 (q, $^2J_{CF}$ = 41 Hz), 114.5 (q, CF_3, $^1J_{CF}$ = 285.8 Hz), 77.1, 38.8, 36.7, 33.4, 27.8. GC/MS *m/z* (rel. intensity): 262 (1, M^+), 149 (7), 135 (100), 107 (23), 93 (29), 79 (34), 69 (30). Anal. calcd for $C_{13}H_{17}F_3O_2$: C, 59.53; H, 6.53. Found: C, 59.49; H, 6.51. For properties of trifluoroacetates, see: Asadullah, M.; Kitamura, T.; Fujiwara, Y. *J. Catal.* **2000**, *195*, 180 (cyclopentyl-, cyclohexyl-, cycloheptyl-trifluoroacetates). Begue, J.-P.; Rock, M. H. *J. Organomet. Chem.* **1995**, *489*, C7 (cyclohexylmethyl trifluoroacetate); Creary, X.; Jiang, Z. *J. Org. Chem.* **1996**, *61*, 3482 (homoadamant-3-yl trifluoroacetate); Creary, X.; Jiang, Z. *J. Org. Chem.* **1994**, *59*, 5106 (adamant-1-yl trifluoroacetate).
7. **General procedure for decarboxylation**:
Method A: A solution of peroxy acid (1 mmol, >92% purity) in CH_2Cl_2 (6 ml)[8] was added dropwise into well-stirred trifluoroacetic anhydride (6 g, 28.6 mmol) at −20°C. In the case of acids **2–5** 1,4-di(trifluoromethyl)benzene (0.214 g, 1 mmol) was added into trifluoroacetic anhydride as internal standard. Decarboxylation proceeds immediately for acids **5–13**. The conversion of acids **2–5** and products distribution were verified by ^1H NMR analysis of the reaction mixture compared to the signal of 1,4-di(trifluoromethyl)benzene. Work-up procedures for the decarboxylation of acids **6–13** included the evaporation of solvent and the flash chromatography on silica of the residue. Typically 5% solution of ether in pentane was used as an eluting solvent. The yields of products are shown in Table 1.
Method B: Carboxylic acid (1 mmol) was added into freshly distilled trifluoroacetic anhydride (1.26 g, 6 mmol) and stirred at room temperature for 20 min. A solution of TFPAA in TFAA (0.722 g, 2.5 mmol of TFPAA) was then added dropwise into a well-stirred solution of carboxylic acid in freshly distillated TFAAn at −20°C and stirred for another 20 min. Decarboxylation proceeds immediately for acids **5–13**. The conversion of acids **2–5** and the product distribution were verified by ^1H NMR analysis of the reaction mixture compare to signal of 1,4-di(trifluoromethyl)benzene. The work-up procedure for the decarboxylation of acids **6–13** included the addition of CH_2Cl_2 (12 ml) into the reaction mixture, washing with H_2O (4×2 ml) and a saturated solution of NH_4Cl in water and drying over Na_2SO_4. Solvent was evaporated and the residue was purified by column chromatography using 5% solution of ether in pentane as an eluting solvent. The yields of products are shown in Table 1.
Propionyltrifluoroacetyl peroxide (14): at 0°C; ^1H NMR (CF_3COOH, 300 MHz): δ 2.07 (q, J = 7.5 Hz, 2H), 0.77 (t, J = 7.5 Hz, 3H). ^{13}C NMR (CF_3COOH, 75 MHz): δ 171.2, 154.7 (q, $^2J_{CF}$ = 48 Hz), 113.4 (q, $^1J_{CF}$ = 287.8 Hz), 22.5, 7.1. ^{19}F NMR (CF_3COOH, 282.2 MHz, relative to $CFCl_3$): δ −73.3. **2-Methylpropionyltrifluoroacetyl peroxide (15)**: at −40°C; ^1H NMR (CCl_2FCClF_2, 300 MHz): δ 1.78 (h, J = 7.2 Hz, 1H), 0.33 (d, J = 7.2 Hz, 6H). ^{13}C NMR (CCl_2FCClF_2, 75 MHz): δ 162.3, 154.1 (q, $^2J_{CF}$ = 48 Hz), 113.1 (q, $^1J_{CF}$ = 287.8 Hz), 33.2, 17.6. ^{19}F NMR (CCl_2FCClF_2, 282.2 MHz, relative to $CFCl_3$): δ −73.4.
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