A Novel Catalytic Pathway for Perfluoroacyl Peroxide Synthesis
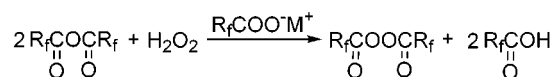
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ABSTRACT

$$2\,R_fCOCR_f + H_2O_2 \xrightarrow{R_fCOO^-M^+} R_fCOOCR_f + 2\,R_fCOH$$

A new catalytic method for synthesis of bis(perfluoroacyl) peroxides (BPFAP) was elaborated by using hydrogen peroxide and perfluoroacyl anhydrides. The desired BPFAP were formed quantitatively in situ when perfluoroacyl anhydride was mixed with hydrogen peroxide (ratio $\geq$ 2:1) in the presence of a catalytic amount of the carboxylate $R_fCOO^-\,M^+$. The essentially irreversible character of this process was shown experimentally and supported on the basis of DFT calculations. The synthesis of new acetyltrifluoroacetyl peroxides is also described.

The chemistry of fluoroalkanoyl peroxides is a well-researched area in organic synthesis, with Hideo Sawada and co-workers leading the effort.[1] Fluoroalkanoyl peroxides manifest unique properties that are attractive not just for fundamental but also for applied chemistry. These peroxides can be used as active radical initiators for the polymerization of halogenated olefins[2] and as reagents for perfluoroalkylation processes of polymers[3] and monomers.[1,4] It has been shown that even polymeric hydrocarbon materials can be perfluorinated with fluoroalkanoyl peroxides.[5] Despite numerous patents[6] and publications[7,8] devoted to fluoroalkanoyl peroxide preparation, a convenient protocol for laboratory

or industrial application remained elusive. Generally, these methods can be summarized (Scheme 1) as the use of

Scheme 1
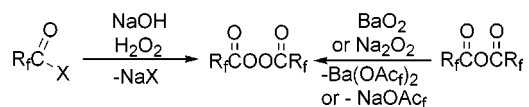
perfluoroacyl chlorides or anhydrides in the presence of water. Moreover, even if the reaction is performed under phase transfer conditions,[6f,7] the hydrolysis and loss of starting reagents, as well as the loss of hydrolyzable bis-(perfluoroacyl) peroxides (BPFAP),[1] occurs in parallel fashion. The formation of salt byproducts is also undesirable.

These literature observations, as well as our experience with trifluoroperacetic acid (TFPAA),[9] led to a research goal of developing a nonaqueous, catalytic, high-yield, and waste-free method for BPFAP synthesis. Understanding the mechanism for the reaction of H_2O_2 with $R_fCOOCOR_f$ was the key to our success. The study of this seemingly obvious

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(4) Ogino, K.; Abe, M.; Morikawa, K.; Mitani, M.; Sawada, H.; Matsumoto, T. *J. Jpn. Soc. Colour M.* **1992**, *65*, 205. Sawada, H.; Mitani, M.; Minoshima, Y.; Nakayama, M. *J. Jpn. Res. Institute M. Technol.* **1994**, *12*, 185.

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(6) (a) Young, D. M.; Stoops, W. N. U.S. Patent 2,792,423, 1957. (b) Bullitt, O. H. U.S. Patent 2,559,630, 1951. (c) Dittman, A. L.; Wringson, J. M. U.S. Patent 2,775,618, 1956. (d) Young D. M. Brit. 794,830, 1958. (e) Miller, W. T.; Dittman, A. L.; Reed, S. K. U.S. Patent 2,580,359, 1951. (f) Sawada, H.; Nakayama, M. JP Patent JP 01249752 A2 19891005, 1989.

(7) Zhao, C.; Zhou, R.; Pan, H.; Jin, X.; Qu, Y.; Wu, C.; Jiang, X. *J. Org. Chem.* **1982**, *47*, 2009.

(8) Sawada, H.; Nakayama, M.; Yoshida, M.; Yoshida, T.; Kamigata, N. *J. Fluorine Chem.* **1990**, *46*, 423.

(9) (a) Krasutsky, P. A.; Kolomitsyn, I. V.; Kiprof, P.; Carlson, R. M.; Fokin, A. A. *J. Org. Chem.* **2000**, *65*, 3926. (b) Krasutsky, P. A.; Kolomitsyn, I. V.; Kiprof, P.; Carlson, R. M.; Sydorenko, N. A.; Fokin, A. A. *J. Org. Chem.* **2001**, *66*, 1701.

reaction was performed with >95% H_2O_2[10] and freshly distilled trifluoroacetic anhydride (TFAAn) with concentration ratios of $[TFAAn]/[H_2O_2] = 0-10$ at room temperature. ^{19}F NMR analyses of the reaction mixtures at different ratios shows the stoichiometric formation of TFPAA (δ −74.3), trifluoroacetic acid (TFAA, δ −77.7), and nonreacted TFAAn (δ −77.1) when the ratio $[TFAAn]/[H_2O_2]$ is greater than 1. When the ratio was greater than 5, only traces of bis(trifluoroacetyl) peroxide[11] (BTFAP, δ −72.8) appeared in the reaction mixture. Nonetheless, the presence of BTFAP in the reaction media indicated the feasibility of BTFAP formation. It was reasonable to infer that acidic or basic catalysis could facilitate this ionic process. Acidic catalysts (H_2SO_4, BF_3) did not change the ratio of components. However, the addition of trace amounts of sodium or potassium salts of TFAA (less than 0.1% of the concentration of H_2O_2), dramatically changed the product distribution. The peak for TFPAA completely disappeared, and the peak for BTFAP appeared when the ratio of $[TFAAn]/[H_2O_2]$ was greater than or equal to 2. The essentially irreversible character of this catalytic, consecutive process was characterized by Figure 1. Figure 1 also demonstrates quantitative transfer of active oxygen from H_2O_2 into TFAAn.
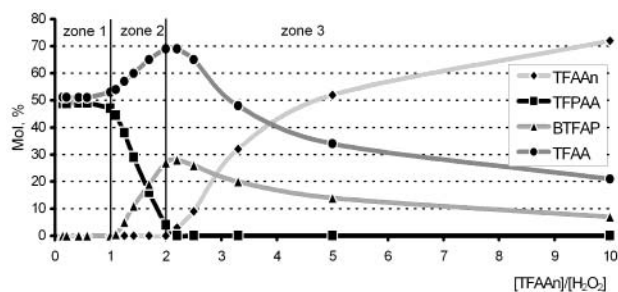

Figure 1. Molar concentration of fluorine-containing products vs. the ratio $[TFAAn]/[H_2O_2]$ in the presence of CF_3COO^-.

The same observation was made for other perfluorinated anhydrides ($R_f = C_2F_5$, C_3F_7, C_4F_9).[12] To clarify accurately the energetic feasibility of this process, DFT computations at the B3LYP/6-31G(d) level, as implemented in a Gaussian 98 program, were employed.[13] The results of these calculations indicated that this process was energetically rather favorable (Scheme 2).

Scheme 2

$\Delta E = -8.9$ kcal/mol
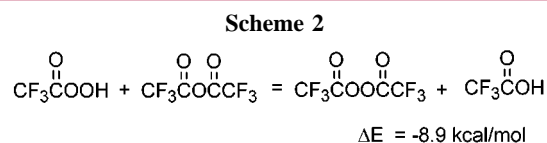
The efficiency of basic catalysis for this process is understandable, because of the higher nucleophilicity of perfluoropercarboxylate ion (R_fCOOO^-) compared to the

corresponding perfluorocarboxylic peracid (R_fCOOOH). The rapid ion exchange process in polar perfluorocarboxylic acid also facilitates the catalytic activity. This result supports accepting a general scheme for BPFAP formation (Scheme 3).

Scheme 3

$R_f = CF_3$, C_2F_5, C_3F_7, C_4F_9
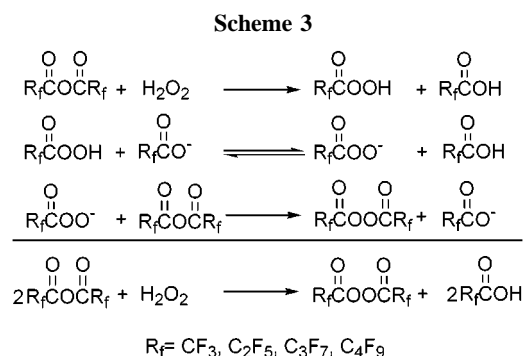
The stoichiometry of the entire process (Scheme 3) shows that the ratio of [bis(perfluoroacyl) anhydride]/$[H_2O_2]$ should be equal to 2 (if 100% H_2O_2) in order to receive the highest concentration of BPFAP. If the ratio of [bis(perfluoroacyl) anhydride]/$[H_2O_2]$ is less than or equal to 1 (zone 1), an equivalent amount of perfluorocarboxylic peracid and perfluorocarboxylic acid is formed. If this ratio is greater than 1 and less than 2 (zone 2), the solution would contain perfluorocarboxylic peracid, BPFAP, and perfluorocarboxylic acid. When this ratio is greater than 2 (zone 3), the solution

(10) Pizey, S. J. *Synthetic Reagents*; John Wiley & Sons: New York, 1985; Vol. 6, p 60.

(11) Kopitzky, R.; Willner, H.; Hermann, A.; Oberhammer, H. *Inorg. Chem.* **2001**, *40*, 2693.

(12) **General procedure** for the preparation of a solution of bis-(perfluoroacyl) peroxide (BPFAP) in the corresponding perfluorocarboxylic acid: 95% H_2O_2 (1.70 g, 47.5 mmol H_2O_2) was added dropwise into a well-stirred solution of R_fCOOK (0.047 mmol) in freshly distilled bis-(perfluoroacyl) anhydride (100 mmol) at 0 °C. After addition of the H_2O_2, the reaction mixture was stirred for 10 min at 0 °C. A 31% (mol) solution of BPFAP in perfluorocarboxylic acid was obtained. It is possible to use less concentrated H_2O_2. In this case the solution of bis(perfluoroacyl) peroxide in perfluorocarboxylic acid would be less concentrated to a corresponding degree. For example 8% (mol) solution of BPFAP in perfluorocarboxylic acid was obtained when 30% H_2O_2 (1.77 g, 15.6 mmol H_2O_2) was added dropwise into a well-stirred solution of R_fCOOK (0.047 mmol) in freshly distilled bis(perfluoroacyl) anhydride (100 mmol) at 0 °C. After addition of the H_2O_2, the reaction mixture was stirred for 10 min at 0 °C. The concentration of BPFAP was measured by ^{19}F NMR spectra. [19]F chemical shifts are given relative to external $CFCl_3$. BTFAP ^{19}F NMR (CF_3COOH, 282.2 MHz): δ −72.8. Bis(pentafluoropropanonyl) peroxide ^{19}F NMR (C_2F_5COOH, 282.2 MHz): δ −85.1, −121.3. Bis(heptafluoro-butanoyl) peroxide ^{19}F NMR (C_3F_7COOH, 282.2 MHz): δ −82.6, −118.4, −128.2. Bis(nonafluoropentanoyl) peroxide ^{19}F NMR (C_4F_9COOH, 282.2 MHz): −83.2, −117.9, −124.8, −127.5.
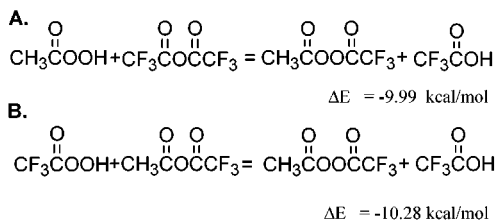
(13) *Gaussian 98*, revision A.5; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J., Jr. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1998.

will contain BPFAP, bis(perfluoroacyl) anhydride, and perfluorocarboxylic acid (see Figure 1). When freshly distilled bis(perfluoroacyl) anhydride is used, the formation of BPFAP was not observed.[14] Knowledge about this peculiarity of the reaction between H_2O_2 and bis(perfluoro-acyl) anhydrides is very important for planning synthetic operations. For instance, zone 1 may be explored for epoxidation,[15] Baeyer−Villiger[16] reactions, and Criegee[9] rearrangement processes. Zone 2 is rather unpredictable, because two different processes are the possible (radical[1−5] reactions may be caused by the presence of BPFAP). Zone 3 should be interesting for studying radical reactions of BPFAP in the corresponding perfluorocarboxylic acid.

BTFAP manifests high stability in TFAA. Thus, the concentration of a 28% solution of BTFAP in TFAA remained essentially unchanged (26.5%) at −10 °C for 6 months. It is known that the stabilities of other BPFAP are lower,[8,17] but they are also sufficiently stable for industrial/laboratory safe operations when maintained at −10 °C in the corresponding perfluorinated acid.

The synthesis of asymmetric alkyloylperfluoroacyl per-oxides was the next logical step of the research. A literature search showed the absence of any information on this area. Our research was directed to the synthesis of acetyltrifluoro-acetyl peroxide,[9a] as the first member of this class of asymmetric perfluoroacyl peroxides. Two possible ways for this peroxide synthesis were proposed on the basis of our experience with re-esterification processes (Scheme 4). One

Scheme 4

A.
$$CH_3COOH + CF_3COCCF_3 = CH_3COOCCF_3 + CF_3COH$$

$$\Delta E = -9.99 \text{ kcal/mol}$$

B.
$$CF_3COOH + CH_3COCCF_3 = CH_3COOCCF_3 + CF_3COH$$

$$\Delta E = -10.28 \text{ kcal/mol}$$

method involves peracetic acid and TFAAn (**A**), and the other involves TFPAA and acyltrifluoroacyl anhydride (**B**).[9a] The DFT computational analysis at the B3LYP/6-31G(d) level[13] (Scheme 4) shows that these reactions are energetically even more favorable ($\Delta\Delta E = 1.09−1.38$ kcal/mol) than described in Scheme 2. These thermodynamic calculations were quite promising for the preparation of acetyltrifluoroacetyl per-oxide. A solution of peracetic acid, which was prepared by the Swern procedure,[18] was added at 0 °C into TFAAn in TFAA (method **A**, Scheme 4). Acetyltrifluoroacetyl peroxide

(14) TFAAn contains traces of sodium trifluoroacetate if stored for a long time in glass. This concentration may be sufficient to effectively catalyze BTFAP formation (Scheme 3).

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(16) Renz, M.; Meunier, B. *Eur. J. Org. Chem.* **1999**, 737.

(17) Sawada, H. *Rev. Heteroatom Chem.* **1993**, *50*, 205. Sawada, H.; Nakayama, M.; Kikuchi, O.; Yokoyama, Y. *J. Fluorine Chem.* **1990**, *50*, 393.

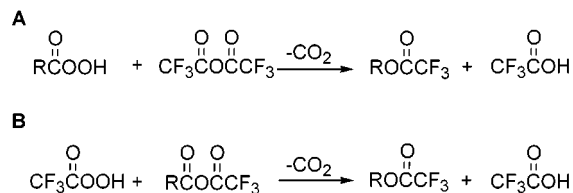(18) *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1970; Vol. 1, pp 475−516.

can also be prepared[9a] by adding a solution of TFPAA in TFAA at 0 °C into a solution of acetic acid in freshly distilled TFAAn (method **B**, Scheme 4). ^{1}H and ^{19}F NMR analysis of the reaction mixture shows the formation of acetyltrif-luoroacetyl peroxide[9a] in a quantitative yield. The initial active oxygen was preserved in both methods **A** and **B**. Identical spectral data were obtained for acetyltrifluoroacetyl peroxide, when the acyl cation was generated in TFPAA (Scheme 5).[9a] This approach should be considered as the third method for in situ acetyltrifluoroacetyl peroxide generation.

Scheme 5
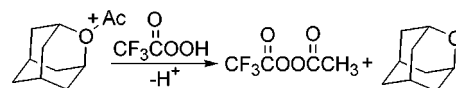
A solution of acetyltrifluoroacetyl peroxide in TFAA was stable at 0 °C without noticeable changes in the NMR spectra or in the concentration of active oxygen. Attempts to use methods **A** and **B** for other carboxylic acids (propanoic, *i*-butanoic, pivalic, etc.) did not lead to stable peroxides because of their rapid decomposition to the corresponding trifluoroacetates (Scheme 6).

Scheme 6

A
$$RCOOH + CF_3COCCF_3 \xrightarrow{-CO_2} ROCCF_3 + CF_3COH$$

B
$$CF_3COOH + RCOCCF_3 \xrightarrow{-CO_2} ROCCF_3 + CF_3COH$$

This new method for selective, nonradical decomposition of alkanoyltrifluoroacetyl peroxides and the corresponding mechanism will receive additional consideration in a fol-lowing paper. At this point we may note that both methods **A** and **B** (Scheme 6) do not require any basic catalysis. This can be explained by the enhanced nucleophilicity[19] of carboxylic peracids compared to perfluorocarboxylic per-acids.

Supporting Information Available: ^{19}F NMR spectral characterization of bis(perfluoroacyl) peroxides and tables containing absolute energies and *x,y,z*-coordinates of all computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) (a) Hjelmeland, L. M.; Loew, G. *Tetrahedron* **1977**, *33*, 1029. (b) Fehr, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 2407.