FLUORINATED PEROXIDES DERIVED FROM HEXAFLUOROACETONE. I. INSERTION OF $(CF_3)_2CO$ INTO HYDROPEROXIDES

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SUMMARY

The new fluorinated peroxides $HOC(CF_3)_2OOH$, $HOC(CF_3)_2OOC(CF_3)_2OH$, and $(CH_3)_3COOC(CF_3)_2OH$ have been prepared by the insertion of hexafluoroacetone into the O-H bonds of hydrogen peroxide and t-butyl hydroperoxide. In addition, the alkali metal salts $HOC(CF_3)_2OOM$ (M=Li or Na) and $(CH_3)_3COOC(CF_3)_2ONa$ have been prepared by neutralization of the corresponding protonic compound with the appropriate metal hydride.

The new compounds are safer (i.e., less flammable and less explosive) than analogous or similar hydrocarbon peroxides, though they are somewhat less thermally stable than the parent hydroperoxides.

INTRODUCTION

Some time ago we initiated a study of the synthesis and characterization of organoperoxides in which the organic substituents were highly or, in many cases, entirely fluorine-substituted. The expectation was that such materials would be useful as free radical polymerization initiators and that they would also be generally safer (i.e., less explosive and

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less flammable) than the peroxides normally used for this purpose.
It was also recognized that aliphatic fluorinated peroxides repre-
sent a third, and heretofore little studied, general type of free
radical polymerization initiator. The other principal groups in
such a classification consist of the well known organic peroxides
with both "fuel" (C-H bonds) and "oxidizer" (O-O bonds) in the
same molecule, a circumstance which often leads to dangerous
instability, and the various azo initiators in which the "oxidi-
zer" portion of the molecule has been replaced by an azo group
while the hydrocarbon "fuel" portion is retained. The fluorinated
peroxides complete the set by maintaining the peroxide linkage
while having non-oxidizable fluorocarbon groups substituted for
the hydrocarbon moieties.

Furthermore, it seemed likely that fluorinated aliphatic
peroxides could be prepared so as to encompass a complete spec-
trum of stabilities (i.e., of initiator activity) ranging from
very low, as in FOOF (unstable even at -160°) [1], to very high,
as in CF_3OOCF_3 (prepared at 265°) [2]. Even more intriguing was
the possibility of using fluorine to stabilize peroxidic struc-
tures for which no hydrocarbon counterparts are known. We have
previously reported one such compound, CF_3OOOCF_3 [3], which was
prepared at the beginning of this work.

Although various isolated examples of fluorinated peroxides
were known at the time this work was initiated, few of these
were the result of studies directed toward their synthesis and
properties as a class. Notable contributions had been made,
however, by Cady [4-6] and more recently by Des Marteau [7-9],
who has been particularly active in preparing compounds with
the CF_3OO- grouping. An excellent review of fluorinated per-
oxides and their chemistry has recently been published by
De Marco and Shreeve [10]. In general, the fluorinated per-
oxides hitherto considered have been relatively simple structures
derived from highly energetic and experimentally difficult re-
action sequences (use of F_2, ClF, OF_2, hypofluorites, etc.)
which severely limit the fluorocarbon substituents which may
be incorporated.

A seemingly reasonable and versatile approach to the preparation of a variety of related fluorinated peroxides for comparative studies, and one which would circumvent the limitations cited above, would be to make use of the well known insertion reactions of hexafluoroacetone (into OH bonds, for example) and to determine whether these could be extended to hydrogen peroxide and its derivatives.

EXPERIMENTAL

Caution: Although no explosions have been observed in the course of extensive handling of these compounds, it should be remembered that they are peroxides and should be handled only in small quantities and with care and adequate shielding. Hydrogen peroxide (98%) must be handled with extreme care and kept from all combustible materials.

HOC(CF₃)₂OOH [11]

In a typical experiment, 98% H_2O_2 (2.0 g, 58.8 mmoles) from FMC Corporation was introduced, using a glass syringe and a Kel-F needle attachment, into a 50 ml all glass reaction tube fitted with a Fischer-Porter Teflon valve. The Kel-F needle attachment allowed removal of the strong H_2O_2 from its original container without fear of metal-catalyzed decomposition and was flexible enough to permit introduction directly into the reactor through the valve after the Teflon plug was removed.

After degassing the hydrogen peroxide by alternate freezing, pumping, and thawing cycles on the vacuum system, a slight excess (60-65 mmoles) of gaseous $(CF_3)_2CO$ was allowed to contact the hydrogen peroxide. Rapid uptake of the gas was shown by a decrease in the pressure. After the pressure had ceased to fall, quick pumping at room temperature removed excess $(CF_3)_2CO$.

The material was determined to have the indicated formulation by measurement of the amount of hexafluoroacetone absorbed per unit weight of hydrogen peroxide, by demonstrating that the

^{19}F and ^{1}H nmr spectrum consisted of a singlet at 79.1 Ø and a broad adsorption (due to rapid exchange) at $\delta=8.83$ respectively, and by establishing via KI titer that the oxidizing power corresponded to that expected for $HOC(CF_3)_2OOH$ of 97.02% purity.

$HOC(CF_3)_2OOC(CF_3)_2OH$

The ^{19}F nmr spectrum of a mixture of hexafluoroacetone and H_2O_2 (98%) was measured in a 3/16" O.D. Kel-F nmr tube equipped with a removable metal valve and therefore suitable for the introduction and removal of both H_2O_2 and $(CF_3)_2CO$. The initial spectrum consisted of three singlet peaks at +78.4; +78.6; and +83.9 ppm (relative to $CFCl_3$) which were assigned to $HOC(CF_3)_2OOC(CF_3)_2OH$, $HO(CF_3)_2OOH$, and $HOC(CF_3)_2OH$ respectively. This assignment was confirmed by the addition of H_2O_2 which caused an increase in the +78.6 ppm peak at the expense of the +78.4 ppm peak, indicating that the following transformation had occurred:

$$HOC(CF_3)_2OOC(CF_3)_2OH + H_2O_2 \rightarrow 2HOC(CF_3)_2OOH$$
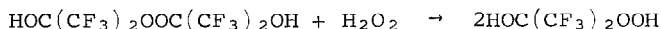
On the other hand, addition of $(CF_3)_2CO$ led to the appearance of a new peak downfield from the +78.4 peak which was assigned to $(CF_3)_2CO$. The peak associated with the 2:1 adduct was enhanced and the peak associated with 1:1 adduct was almost obliterated as a consequence of the reaction:

$$HOC(CF_3)_2OOH + (CF_3)_2CO \rightarrow HOC(CF_3)_2OOC(CF_3)_2OH$$

Throughout the experiment, the peak associated with the hexafluoroacetone hydrate, $HOC(CF_3)_2OH$, remained relatively unchanged.

The new material, $HOC(CF_3)_2OOC(CF_3)_2OH$, is unstable with respect to loss of $(CF_3)_2CO$; evacuation converts all the material to $HOC(CF_3)_2OOH$ which does not lose $(CF_3)_2CO$ at room temperature.

$(CH_3)_3COOC(CF_3)_2OH$

Lucidol's t-butyl hydroperoxide-90, containing about equal parts of $(CH_3)_3COH$ and H_2O as impurities, was treated with an overpressure (less than 1 atm) of $(CF_3)_2CO$. This led to the rapid uptake of the ketone and a large increase in liquid volume. After a period of time the liquid became yellow and was pumped into a trap, leaving behind a few crystals of a yellow solid having no oxidizing power (KI test) which was not identified. The resulting liquid was fractionated several times (-23°) leaving no residue in the fractionation or transfers. The -23° fraction was then overpressured with more $(CF_3)_2CO$. After overnight treatment with the ketone, evaporation of the material led to the desired product. Calculated for $(CH_3)_3COOC(CF_3)_2OH$: %C, 32.80; %F, 44.29; Found: %C, 32.60; %F, 45.00.

Aqueous potassium iodide tests confirmed that the material is a peroxide, but the appearance of the iodine color is quite slow. However, it is speeded by the addition of acetone, probably because of enhanced solubility.

$NaOOC(CF_3)_2OH$

Sodium hydride (.96 g; 40 mmoles) was charged to a 50 ml glass reactor containing a magnetic stirbar and fitted with a Kontes glass/Teflon valve, a dropping funnel, and a drying tube as pressure relief valve. The reactor was outgassed and ~30 ml of $CF_2ClCFCl_2$ to serve as diluent/dispersant was condensed in at -196°. The reactor was warmed to 0°C and $HOC(CF_3)_2OOH$ (10 gms; 50 mmoles) was added slowly through the dropping funnel Hydrogen was evolved and allowed to escape through the drying tube. A white slurry resulted. After the evolution of hydrogen had stopped, the mixture (which was quite thick) was stirred for another hour, and volatile materials were removed by pumping overnight. A fluffy white powder of $NaOOC(CF_3)_2OH$ resulted. Analytical: Calculated for $HOC(CF_3)_2OONa$; %C, 16.22; %F, 51.35; %Na, 10.36. Found %C, 15.66; %F, 49.50; %Na, 11.05.

The potassium iodide titer was found to be equivalent to that of $HOC(CF_3)_2OONa$ of 97.5% purity.

$LiOOC(CF_3)_2OH$

A reaction was carried out between $HOOC(CF_3)_2OH$ and LiH in CCl_3F. The starting hydroperoxide was prepared according to the method described above; in several experiments, titers invariably indicated greater than 95% purity for the $HOC(CF_3)_2OOH$. A slurry of LiH (.48 g; 60 mmole) in CCl_3F was prepared and cooled to 0°. The $HOOC(CF_3)_2OH$ (6.0 g; 30 mmole) was added dropwise to the slurry, resulting in immediate evolution of H_2. The pressure was monitored until one atmosphere was reached, at which time excess gas was allowed to escape through a drying tube packed with indicating Drierite. At the completion of the hydroperoxide addition, the CCl_3F was removed by vacuum techniques, leaving a white solid. It was observed that neither LiH nor the salt product had observable solubility in CCl_3F.

In a second experiment involving a slight excess of hydride, the LiH was suspended in diethyl ether and cooled to 0°. Again the hydroperoxide was added dropwise to the cooled slurry. In contrast to the CCl_3F system, evolution of H_2 at 0° was very slow. The system was allowed to warm to room temperature where H_2 was evolved at a faster, but controlled, rate. As the reaction proceeded, the decrease of LiH was readily observed because the product proved soluble in ether. After 20 hours the solution was filtered in vacuo to remove LiH, and the ether was removed by pumping. Residual amounts of solvent adhered to the salt, but facilitation of ether removal was accomplished by addition of CCl_3F followed by further vacuum drying.

Analysis of the salt prepared in diethyl ether was accomplished by C, F, and Li determinations. Theoretical values for the dilithium salt $LiOOC(CF_3)_2OLi$ are C, 17.00; F, 53.79; and Li, 6.54%. For the monolithium salt $LiOOC(CF_3)_2OH$, the corresponding theoretical values are 17.49; 55.34; and 3.36%. Experimental values were as follows: C, 17.00; F, 53.20; Li, 3.60%. The elemental analysis data are not conclusive but

favor, primarily on the basis of the lithium values, the mono-
lithium salt. Moreover, a representative sample of the solid
product isolated from a 2:1 reaction in $CF_2ClCCFCl_2$ was hydro-
lyzed, and the amount of non-condensable gas (H_2) which was
collected indicated that only half of the LiH had reacted. It
is therefore assumed that the dilithium salt was not formed in
either the CCl_3F or ether solvent.

RESULTS AND DISCUSSION

The insertion of hexafluoroacetone into the oxygen-hydrogen
bond of hydroperoxides in general seems to be facile and to pro-
vide a convenient synthetic approach to the preparation of new
fluorinated peroxides; from the results obtained to date, it is
apparent that this reaction could be extended to a much larger
number of hydroperoxides than have been described here.

The simplest such peroxide based upon hexafluoroacetone
results from its interaction with hydrogen peroxide (the nominal
precursor to all peroxides) to give $HOC(CF_3)_2OOH$. However,
there seemed to be no a priori reason that reaction of hexa-
fluoroacetone with hydrogen peroxide should stop at the insertion
of only one $(CF_3)_2CO$ group, since the resulting material still
contained an -OOH grouping which should be active to further
insertion. As indicated in the experimental section, insertion
of the second $(CF_3)_2CO$ group was subsequently achieved, but the
product was stable only under a pressure of hexafluoroacetone,
and we therefore undertook no further work with this material
beyond the nmr characterization. Chambers and Clark [11] have
also found indications that a greater than 1:1 ratio of hexa-
fluoroacetone could be absorbed by hydrogen peroxide but did
not attempt to isolate nor identify the higher adduct.

In order to extend this line of investigation, and in order
to have a bifunctional derivative which would be useful in fur-
ther reactions, the synthesis of $NaOC(CF_3)_2OONa$ from the reac-
tion of $HOC(CF_3)_2OOH$ with NaH was attempted many times. How-
ever, complete reaction of all the NaH was never achieved, and
only the mono-sodium salt was obtained. Use of the smaller

more hydrogen-like lithium also led only to the mono-metal salt.
It seems quite unusual that both protons, which should be quite
acidic, do not react with the hydride.

It has been tacitly assumed here that the mono-metal salts
which we have prepared are $MOOC(CF_3)_3OH$ and not $HOOC(CF_3)_2OM$ or
a mixture of the two materials. The former seems more likely
since the hydroperoxide functions would be expected to be more
acidic and less sterically hindered than the corresponding
hydroxy compounds and therefore would be expected to react more
rapidly with the basic metal hydride. Moreover, the $HOC(CF_3)_2OO^-$
anion should be inherently more stable than the $HOOC(CF_3)_2O^-$
anion. The latter might be expected to either rearrange to the
more stable $HOC(CF_3)_2OO^-$ or to extrude $(CF_3)_2CO$ to give HOO^-.
Admittedly, however, the $MOOC(CF_3)_2OH$ formulation is open to
question, and we have not pursued it to an absolute conclusion.

An unexpected observation made during the course of this
investigation was that the incorporation of hexafluoroacetone
into a hydroperoxide invariably lowers the stability of the
product fluorinated peroxide at any given temperature. Thus,
our experiments show $HOC(CF_3)_2OOC(CF_3)_2OH$ (unstable at 25°) to
be significantly less stable than $HOC(CF_3)_2OOH$. Moreover,
$HOC(CF_3)_2OOH$ (significant decomposition at 100°) is in turn
less thermally stable than $HOOH$ (B.Pt. 150.2°). Further,
$(CH_3)_3COOC(CF_3)_2OH$ (significant decomposition at 100-110°)
decomposes at a somewhat lower temperature than $(CH_3)_3COOH$
(90%) which has a half-life of around 20 days at 130° [12].
These results are apparently general and contrary to our some-
what naive expectation that the incorporation of electron with-
drawing trifluoromethyl groups would relieve somewhat the inter-
electronic repulsions between the non-bonded electrons of the
oxygen atoms of the peroxide and therefore make it more stable
toward thermal decomposition. Obviously, the situation is
somewhat more complicated than this.

On the other hand, despite the reduced thermal stabilities,
these new materials in which the oxidizable hydrocarbon consti-
tutes a significantly smaller portion of the entire molecule are
apparently less flammable and less explosive than their counter-

parts which have no hexafluoroacetone incorporated. We lack quantitative data to support this point but at no time in extensive work with the compounds described in this paper did we have any sudden decomposition or explosion. Moreover, we have demonstrated that $(CH_3)_3COOC(CF_3)_2OH$ can be ignited but (on a small scale at least) is self-extinguishing, while t-butyl hydroperoxide $(CH_3)_3COOH$, which differs only in having no hexafluoroacetone incorporated, is extremely flammable and burns brilliantly until it is entirely consumed. As a further example, the addition product of H_2O_2 and hexafluoroacetone contrasts markedly with that derived from acetone and hydrogen peroxide. Although $HOC(CH_3)_2OOH$ can be prepared as one of the products of the reaction of acetone with hydrogen peroxide, the mixture is dangerously explosive and, in the usual case, a mixture of many complex peroxides results from further condensation of the $HOC(CH_3)_2OOH$.

The new materials described here may be properly considered to point the way to the preparation of many compounds having the general structure $ROOC(CF_3)_2OM$ (where M=H or alkali metal). These in turn are expected to be useful as fundamental building materials for the preparation of a large number of partially or fully fluorinated covalent peroxides which may have new and/or unexpected properties. Subsequent papers in this series will develop this theme more fully.

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