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FLUORINATED PEROXIDES DERIVED FROM HEXAFLUOROACETONE.
II. INSERTION OF $(CF_3)_2CO$ INTO ALKALI-METAL PEROXIDES AND
SUBSEQUENT REACTION WITH ACTIVE HALOGEN COMPOUNDS

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SUMMARY

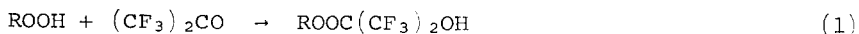
The novel alkali metal peroxide derivatives $(CH_3)_3COOC-$
 $(CF_3)_2ONa$, $NaOC(CF_3)_2OOC(CF_3)_2ONa$ and $CF_3C(O)OOC(CF_3)_2ONa$ have
been prepared through reactions of hexafluoroacetone, $(CF_3)_2CO$,
with the sodium salts of various organic hydroperoxides. These
new salts are soluble in water and polar organic solvents and
have been used to prepare the new covalent fluorocarbon/hydro-
carbon peroxides [$(CH_3)_3COOC(CF_3)_2OC(O)C_6H_5$, $(CH_3)_3SiOC(CF_3)_2-$
 $OOC(CF_3)_2OSi(CH_3)_3$, and $(CH_3)_3COOC(CF_3)_2C(O)CF_3$] through reac-
tion with compounds having active halogen. Although the new
peroxides are apparently less flammable and explosive than their
hydrocarbon analogs, they also exhibit shorter half-lives than
the parent compound (i.e., the peroxide without hexafluoroace-
tone insertion).

INTRODUCTION

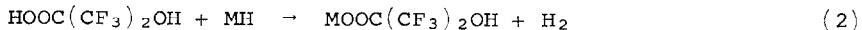
In the first paper of this series [1], we demonstrated
that a number of highly fluorinated peroxide derivatives could
be obtained by the facile insertion of hexafluoroacetone into the
O-H bonds of various hydroperoxides,

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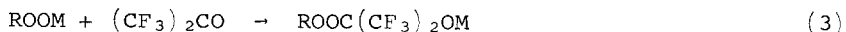
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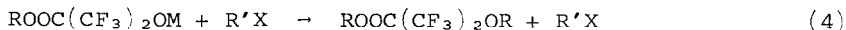
and that in the special case where R=H, alkali metal peroxy-derivatives were obtainable:



However, in order to achieve a wider variety of fluorocarbon/hydrocarbon peroxide structural types, it was of interest to examine the insertion of hexafluoroacetone directly into alkali metal-organoperoxy functions



to obtain products with an active metal salt functionality separate from the peroxy-grouping. Such materials would not only be of interest as a new class of water-soluble free radical initiators, but would serve as intermediates to a wide variety of mixed peroxides via reaction with active halogen compounds:



EXPERIMENTAL

Caution: Although we have experienced no explosions during extensive handling of the materials described here, it should be noted that they are peroxides and should be used only in small quantities and with adequate shielding.

(CH₃)₃COOC(CF₃)₂ONa

Lucidol's t-butyl hydroperoxide-90 was vacuum distilled (b.pt.₂₀=39-40°) to obtain pure (CH₃)₃COOH. A slight excess (11.8 ml) of this material was then added slowly to a slurry of NaH (2 g) in CFCl₃ (~250 ml) at 0° which was contained in a 500 ml flask fitted with a dropping funnel and a pressure relief tube filled with Drierite. A fluffy white solid, (CH₃)₃COONa, was formed and the hydrogen which was evolved was allowed to pass from the system through the drying tube. When reaction was complete, the liquid CFCl₃ and excess (CH₃)₃COOH were removed under vacuum at room temperature, and dry CH₃CN (~200 ml) was added to the remaining white solid to form a slurry. Subsequent addition of (CF₃)₂CO to a pressure of about

one atmosphere led to the rapid absorption of the hexafluoroacetone and dissolution of the solid mass. The slightly yellow liquid was treated with decolorizing carbon and evaporated to dryness. The resulting solid was dissolved in CH_2Cl_2 , filtered to remove insoluble material, and evaporated to leave a residue of $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{ONa}$ (16.25 gms; 76%). The material is a white solid (M.P.= 86°), oxidizing toward KI, and very soluble in CH_3CN and water. It is not rapidly hydrolyzed in water. Calculated for $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{ONa}$: %C, 30.22; %F, 41.01; Found: %C, 29.91; %F, 40.00. The ^{19}F and ^1H nmr spectra consist of singlets at $\delta=78.6$ and 1.25δ respectively.

$\text{CF}_3\text{C}(\text{O})\text{OOC}(\text{CF}_3)_2\text{ONa}$

$\text{CF}_3\text{C}(\text{O})\text{Cl}$ (5.6 g; 50 mmoles) was added slowly to a slurry of Na_2O_2 (4.0 g; 51 mmoles) in CH_3CN (20 ml) in a 100 ml reactor equipped with an adapter and side arm with glass frit and receiver which permitted filtering without exposure to the atmosphere. Reaction occurred rapidly with the concurrent formation of a white precipitate of NaCl, with the $\text{CF}_3\text{C}(\text{O})\text{ONa}$ remaining in solution. Without filtering, $(\text{CF}_3)_2\text{CO}$ (1 atmosphere pressure), was added to the stirring mixture. Although there was no marked change in appearance of the mixture, the ketone was rapidly absorbed and addition was continued until no further absorption occurred. The mixture was then filtered through the glass frit to remove the NaCl and the clear filtrate evaporated to dryness in vacuo to produce $\text{CF}_3\text{C}(\text{O})\text{OOC}(\text{CF}_3)_2\text{ONa}$. The new compound is a white solid oxidizing toward KI and soluble in CH_3CN and water. However, the analytical results indicated high carbon and low fluorine.

A portion of this solid was then introduced into a round-bottomed Fischer-Porter pressure tube (Dry Box operation), dry CH_3CN was added, and enough hexafluoroacetone was introduced to provide a liquid phase at room temperature. The mixture was stirred for several days and then evaporated to dryness, followed by overnight pumping on the solid. A re-analysis gave the following results:

Calculated for $\text{CF}_3\text{C}(\text{O})\text{OOC}(\text{CF}_3)_2\text{ONa}$: %C, 18.86; %F, 53.77; Found: %C, 18.52; %F, 53.00. Presumably, the poor initial results were

due to failure to complete the addition of $(\text{CF}_3)_2\text{CO}$ followed by a failure to completely remove all the CH_3CN .

The ^{19}F nmr spectrum consists of singlets at $\delta=75.1$ and 82.4 for the $-\text{C}(\text{CF}_3)_2-$ and CF_3- groups respectively.

Attempted Preparation of $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OOC}(\text{CF}_3)_2\text{ONa}$

Sodium perbenzoate was prepared as follows: Commercial benzoyl peroxide (containing 20-25% H_2O) was recrystallized from a saturated chloroform solution by the addition of CH_3OH . The pure dried material was then dissolved in CHCl_3 and sodium ethoxide solution (freshly prepared from anhydrous ethanol and sodium) was slowly added to 0° . A white precipitate of $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OONa}$ formed immediately. After completion of the addition the solid was removed from the flask, filtered, and washed with CHCl_3 to remove $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OC}_2\text{H}_5$.

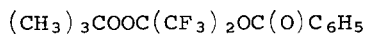
Adsorbed alcohol was then removed under vacuum to leave white solid $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OONa}$. A small sample (2 g) of the $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OONa}$ was placed in a 100 ml round bottom flask with a stir bar and ~10 ml of CH_3CN was added. The mixture was outgassed thoroughly and one atmosphere of $(\text{CF}_3)_2\text{CO}$ was added as an overpressure to the stirring mixture. However, solution did not occur as in the case of the $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{ONa}$ preparation, and very little ketone was absorbed. Evaporation of the CH_3CN gave a white solid which contained no fluorine and appeared to be mainly sodium perbenzoate. For reasons which are not apparent, the preparation of $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OOC}(\text{CF}_3)_2\text{ONa}$ via reaction of $\text{C}_6\text{H}_5\text{C}(\text{O})\text{OONa}$ with $(\text{CF}_3)_2\text{CO}$ clearly does not proceed to a measurable extent under the conditions employed.

$\text{NaOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$

Initial attempts to prepare this salt, using Na_2O_2 and $(\text{CF}_3)_2\text{CO}$ alone, indicated that slow absorption of $(\text{CF}_3)_2\text{CO}$ did indeed occur and that it probably proceeded beyond the 1:1 adduct. Because of the slowness of the reaction, however, a solvent (CH_3CN) was employed in later experiments and improved the process considerably. In a typical experiment, a weighed amount

of Na_2O_2 (3.99 g; 50 mmoles) was introduced into a Fischer-Porter Aerosol Compatibility jar, excess $(\text{CF}_3)_2\text{CO}$ was condensed in, and the mixture was agitated with a Teflon-coated magnetic stir-bar. After 2-3 days the solid had all dissolved until only a slight haziness remained. Evaporation of the CH_3CN at room temperature led to a dry, white solid residue of $\text{NaOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$ which exhibited the expected very strong oxidizing power. Calculated for $\text{NaOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$: %C, 16.95; %F, 53.75. Found: %C, 17.56; %F, 55.60.

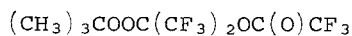
The material is apparently indefinitely stable at room temperature in a dry atmosphere and decomposed only slowly at 85° with the evolution of $(\text{CF}_3)_2\text{CO}$. No oxygen evolution was detected, but the remaining solid has no oxidizing power and was identified as primarily $\text{CF}_3\text{C}(\text{O})\text{ONa}$ and not the expected $\text{NaOC}(\text{CF}_3)_2\text{ONa}$. The $\text{Na}_2\text{OC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$ is extremely soluble in water, CH_3CN , and other polar organic solvents but not in CH_2Cl_2 , pentane or non-polar organic solvents. No solvent or combination of solvents would allow re-crystallization of this material and accounts for the somewhat larger than usual deviation from theory for the analytical results. However, the analyses along with transformation of the material to the derivative $(\text{CH}_3)_3\text{SiOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{OSi}(\text{CH}_3)_3$, as described below, leave no doubt of its correct formulation.



$(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{ONa}$ (2 g; 7.2 mmoles) was placed in a 100 ml round bottom flask equipped with an adapter with a Teflon stopcock and a dropping funnel. It was dissolved in dry CH_3CN (10 ml) in a dry box operation, and then $\text{C}_6\text{H}_5\text{C}(\text{O})\text{Cl}$ (1.2 g; 8.6 mmoles) was added dropwise to the stirring mixture. Sodium chloride precipitated slowly from the solution, which was stirred at room temperature overnight. Filtration of the mixture to remove sodium chloride was followed by evaporation of the CH_3CN to give a white solid which melted slightly above room temperature and was tentatively identified as $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{OC}(\text{O})\text{C}_6\text{H}_5$. Calculated for $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{OC}(\text{O})\text{C}_6\text{H}_5$: %C, 46.67; %F, 31.67; Found: %C, 47.33; %F, 33.80. Although the analytical results are not precise, in conjunction with

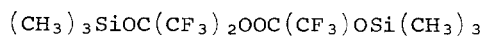
the nmr results, they leave little doubt concerning the new compound's identity.

		Assignment	Chemical Shift	Multiplicity	Relative Intensity
NMR:	^1H	CH_3	1.24	singlet	8.4
		C_6H_5	7.45-8.13	complex	5.6
	^{19}F	CF_3	72.4	singlet	N.A.

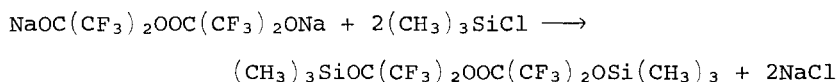


Initial attempts to prepare this compound were made by dissolving the $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{ONa}$ in acetonitrile and presurizing an excess of $\text{CF}_3\text{C}(\text{O})\text{Cl}$ into the reaction flask. Sodium chloride precipitated immediately, but separation of the product from CH_3CN proved difficult by trap-to-trap fractionation. Poor analytical results were obtained probably due to unremoved CH_3CN which would contribute to both the observed high carbon and low fluorine analyses.

A second attempt was made using $\text{CF}_3\text{C}(\text{O})\text{Cl}$ itself as the solvent so that separation from CH_3CN would not be necessary. The $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{ONa}$ was placed in a round bottom flask, excess $\text{CF}_3\text{C}(\text{O})\text{Cl}$ was condensed into it, the mixture was stirred for several hours, and volatile materials were then removed and fractionated. Material retained at -23° was tentatively identified as $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{OC}(\text{O})\text{CF}_3$. A slight yellow color developed in the clear liquid upon standing in the light at room temperature over a period of days but disappeared upon re-fractionation. The material was then stored in the dark at -25° without further discoloration. Elemental analyses were not obtained on this compound, but the KI titer corresponded to a material of composition $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{C}(\text{O})\text{CF}_3$ of greater than 96% purity.



This silicon-containing peroxidic derivative was formed by reaction of the appropriate di-sodium salt with $(\text{CH}_3)_3\text{SiCl}$, as represented by the equation:



For the synthesis, 10 g of $\text{NaOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$ was placed in a 100 ml reactor containing a magnetic stirbar and equipped with a greaseless Kontes valve. Excess $(\text{CH}_3)_3\text{SiCl}$ was syringed into the vessel where the heat of reaction caused the liquid to boil, so the mixture was cooled to 0° . After complete addition, the bath was stirred overnight at room temperature. Fractionation through a -23° trap led to the isolation of a 50% yield of $(\text{CH}_3)_3\text{SiOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{OSi}(\text{CH}_3)_3$, which exhibited the expected oxidizing power toward KI. Calculated for $(\text{CH}_3)_3\text{SiOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{OSi}(\text{CH}_3)_3$: %C, 28.24; %F, 44.7; Found: %C, 28.25; %F, 44.42.

Half-Life Determinations

The half-life determinations were carried out after first "standardizing" the peroxides by dissolving 0.1 g of each in 20 ml acetone, then removing a 5 ml aliquot and adding excess (1 ml) saturated KI and 5 ml acetic acid to develop the iodine color, and then titrating the liberated iodine with standardized thiosulfate; this gave a value for the starting concentration of peroxide at time = 0. Subsequent peroxide concentrations were then obtained after mixtures of peroxide in acetone had been heated in Pyrex tubes sealed by Kontes Teflon stopcocks for varying lengths of time. Normally, four tubes would be sealed with the proper amount of acetone and peroxide, after purging with nitrogen to remove oxygen, and these were then placed in a constant temperature bath. After the appropriate time interval, each tube was then rapidly cooled, opened, and titrated as above to determine peroxide content. The logarithm of the remaining concentration of peroxide was then plotted against the time involved (results were invariably reasonably straight lines) and half-life values were calculated in the usual way. The values obtained are probably not highly accurate, since the reproducibility between runs was not high, but the relative ordering is probably correct.

DISCUSSION

The insertion of hexafluoroacetone into a sodioperoxide, using $(\text{CH}_3)_3\text{COONa}$ and $(\text{CF}_3)_2\text{CO}$, is of course analogous to the previously reported [1] insertion of $(\text{CF}_3)_2\text{CO}$ into $(\text{CF}_3)_3\text{COOH}$, and good yields of $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{ONa}$ are easily obtained. A particularly interesting observation associated with this peroxide is that it is not only soluble in polar solvents such as water and acetonitrile, as would be expected, but is also soluble in non-polar solvents such as pentane. Indeed, it seems least soluble in solvents of intermediate polarity such as methylene chloride. Apparently, significant ion pairing can occur in solvents of low polarity and models suggest that certain configurations are possible in which the sodium atom is well shielded by the organic portions of the molecule.

The failure to achieve direct insertion of hexafluoroacetone into Na_2O_2 is surprising, since it seemed reasonable to expect that the compound $\text{NaOC}(\text{CF}_3)_2\text{OONa}$, analogous to $\text{HOC}(\text{CF}_3)_2\text{-OOH}$ prepared from insertion into H_2O_2 [1], should result. The compound actually formed, $\text{NaOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$, is the analog of the previously prepared but unstable "double insertion" compound $\text{HOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{OH}$ prepared from $(\text{CF}_3)_2\text{CO}$ and HOOH . Possibly the crystal energy of the sodium salt provides sufficient stabilization for its isolation as a solid.

Quite surprisingly, we were unable to prepare the di-sodium or di-lithium analog of $\text{HOC}(\text{CF}_3)_2\text{OOH}$. Neither the direct method using 1:1 stoichiometric ratios of $\text{Na}_2\text{O}_2:(\text{CH}_3)_2\text{CO}$ nor the thermal decomposition of $\text{NaOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$ led to $\text{NaOC}(\text{CF}_3)_2\text{OONa}$. As reported in the previous paper of this series [1], attempts to neutralize both protons of $\text{HOC}(\text{CF}_3)_2\text{OOH}$ with alkali metal hydrides led to replacement of only one, and we have no explanation for this apparent anomaly. Extension of the insertion reaction of hexafluoroacetone into certain other sodioperoxides was relatively straightforward. Thus, $(\text{CF}_3)_2\text{CO}$ inserted readily into $\text{CF}_3\text{C}(\text{O})\text{OONa}$ to give $\text{CF}_3\text{C}(\text{O})\text{OOC}(\text{CF}_3)_2\text{ONa}$. Although the insertion of hexafluoroacetone into ROONa type compounds is reasonably facile, it is not completely general, since there seems to be no absorption of hexafluoroacetone by

sodium perbenzoate. The reason for the inactivity of this particular salt is not known.

The new derivatives described here are similar to those derived previously from the insertion of hexafluoroacetone into hydroperoxides [1] in that they appear to be less hazardous than the parent compounds and hydrocarbon analogs, even though they are less thermally stable than the parent sodio-peroxides. Thus $\text{NaOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$ is much less thermally stable than NaOONa ; $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{ONa}$ is less stable than $(\text{CH}_3)_3\text{COONa}$ and $\text{CF}_3\text{C}(\text{O})\text{OOC}(\text{CF}_3)_2\text{ONa}$ is less stable than $\text{CF}_3\text{C}(\text{O})\text{OONa}$. In each case a principal mode of decomposition of the fluorinated compound is extrusion of hexafluoroacetone.

As expected, these sodium derivatives of fluorinated peroxides are excellent intermediates to a number of covalent fluorinated peroxides derived from reaction with these with acyl chlorides, silyl chlorides or other materials with active halogen. For example, we have successfully prepared several derivatives of $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{ONa}$ and some of $\text{NaOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$.

An important aspect of any new peroxide, insofar as its activity as a free radical initiator is concerned, is its stability as designated by its half-life at a given temperature. This serves to determine whether it is a "fast" or "slow" polymerization catalyst and gives initial direction to the selection of conditions for the study of polymerization reactions.

The half-life determinations for peroxides synthesized in this and the preceding work [1] are given in Table I. From the data, it is clear that the most unstable new peroxide is $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)\text{OC}(\text{O})\text{CF}_3$, followed closely by $\text{NaOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$, while the related material $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{OSi}(\text{CH}_3)_3$ seems to be the most stable. An interesting inference to be drawn from Table I is that the peroxides which differ most in half-life are both derivatives of $(\text{CH}_3)_3\text{COOC}(\text{CF}_3)_2\text{ONa}$. It was unexpected that derivatization at a point so removed from the peroxidic bond would have so profound an effect on the stability.

Not surprisingly, the half-lives of the new alkali metal salts of fluorinated peroxides are pH sensitive. For example, $\text{NaOC}(\text{CF}_3)_2\text{OOC}(\text{CF}_3)_2\text{ONa}$ is much more stable in basic solution

Table I

HALF-LIFE DETERMINATIONS

Peroxide	Temp.	T _{1/2} (Hrs)
(CH ₃) ₃ COOC(CF ₃) ₂ OC(O)CF ₃	40°C	32-1/2
NaO(CF ₃) ₂ COOC(CF ₃) ₂ ONa	45°C	25-1/2
(CH ₃) ₃ SiO(CF ₃) ₂ COOC(CF ₃) ₂ -OSi(CH ₃) ₃	80°C	1-1/4
(CH ₃) ₃ COOC(CF ₃) ₂ ONa	75°C	5-1/2
HO(CF ₃) ₂ COOH [1]	90°C	17-1/4
(CH ₃)COOC(CF ₃) ₂ OH [1]	110°C	1
(CH ₃) ₃ COOC(CF ₃) ₂ OC(O)C ₆ H ₅	120°C	3
(CH ₃) ₃ COOC(CF ₃) ₂ OSi(CH ₃) ₃	120°C	12-1/2
(CH ₃) ₃ COOH-90 [2]	130°C	513

than it is in neutral or acidic solutions. Thus, in buffered solutions at pH 8.0, NaOC(CH₃)₂OOC(CF₃)₂ONa has a half-life of approximately 1 hr. at 5°, but at pH 9.6, it has a half-life of 7 hr. at 25°. This probably results from an inhibition by bases of the hydrolysis of the new peroxide to the relatively unstable HOC(CF₃)OOC(CF₃)₂OH.

It seems clear that the insertion of hexafluoroacetone into ROOH AND ROONa compounds as described in this and in the first paper of this series can lead to a number of compounds of the general form ROOC(CF₃)₂ONa. Such materials can in turn be reacted with a large number of active halogen compounds to produce compounds of the general formula ROOC(CF₃)₂OR' covering a wide range of structures and reactivities. Moreover, combination of bifunctional compound such as NaOC(CF₃)₂OOC(CF₃)₂ONa, with bifunctional active halogen compounds should lead to polymeric and/or cyclic peroxides.

REFERENCES

- 1 L.R. Anderson, C.T. Ratcliffe, D.E. Young, and W.B. Fox, this Journal, submitted for publication.
- 2 Pennwalt-Lucidol Organic Peroxide Bulletin, 8.102, September, 1969.