was concluded that sulfonation of 2,6-lutidine occurred in the 3-position.

The *S*-benzylisothiuronium salts was obtained as an oil which could not be induced to crystallize.

Spectra. The infrared spectra of all the materials were obtained using a Perkin Elmer recording instrument, Model 21, Ser. 140.

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Peroxides. IX. New Method for the Direct Preparation of Aromatic and Aliphatic Peroxy Acids[2]

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A new direct, rapid procedure for the preparation of both aromatic and aliphatic peroxy acids is described. This consists in treating 90–95% hydrogen peroxide with a solution or slurry of carboxylic acid in methanesulfonic acid in mole ratios of 5:3:1 of methanesulfonic acid–hydrogen peroxide–carboxylic acid for most of the peroxy acids for one to three hours of reaction time. Optimum temperatures are generally from 30–40°, but higher operating temperatures (up to 60°) and higher mole ratios of methanesulfonic acid–carboxylic acid (up to 20:1) are useful for carboxylic acids having low solubility in the medium. Insoluble acids can be usefully replaced by their more soluble esters. Labile functional groups present in the acids, such as hydroxyl and cyano, are retained unchanged. For the first time, a method is described for the direct preparation of peroxybenzoic acid from benzoic acid in essentially quantitative yield. Peroxy acids of 93–99% purity in yields of 85–97% are obtained with few exceptions. *m*-Methoxy- and *p*-methoxyperoxybenzoic acids cannot be prepared by this procedure. The stability of several of the solid peroxy acids on storage at 25° for two, four, and eight weeks was determined by peroxide oxygen analysis. An attempt has been made to explain the differences in melting point between peroxy acid and corresponding carboxylic acid.

Since publication of the review on organic peroxy acids,[3] several additional procedures for peroxy acid preparations have been reported. Approximately twenty methods and modifications are now available for peroxy acid synthesis. These methods, with possibly one exception, are not general; only a few are of value as synthetic methods for obtaining high purity peroxy acids of specific types in high yields.

Formation of a peroxy acid from the parent acid and hydrogen peroxide is an equilibrium process[4] in accordance with the equation.

$$RCO_2H + H_2O_2 \rightleftharpoons RCO_3H + H_2O$$

In most cases the rate of peroxy acid formation is impractically slow but is increased by acid catalysts. Advantage was taken of the acid-catalyzed equilibrium reaction by removing water at 40–50° by such azeotropic agents as alkyl acetates and chloroform.[5]

Although this method is reported to be useful for peroxyacetic and peroxypropionic acids, it failed to form longer chain peroxy acids, such as peroxy 2-ethylhexanoic acid. No examples were given for the preparation of aromatic peroxy acids by this method.

The most useful procedure for the direct preparation of long chain aliphatic monobasic[6] and dibasic[7] peroxy acids employs concentrated sulfuric acid as reaction medium and catalyst with 50–65% hydrogen peroxide. This procedure, unfortunately, fails with aromatic acids and certain aliphatic acids containing functional groups sensitive to sulfuric acid. Also, it is limited to monobasic acids up to palmitic acid and dibasic acids up to about 1,10-decanedicarboxylic acid owing to solubility problems. Benzoic, *p*-methoxybenzoic and *p-tert*-butylbenzoic acids violently decompose or carbonize in the presence of concentrated sulfuric acid and concentrated hydrogen peroxide (see Experimental) while *p*-nitrobenzoic[8] and *o*-nitrobenzoic acids give yellow-orange colored compounds containing no active oxygen. Failure of the sulfuric acid method may be attributed to its strong oxidation-sulfonation properties and low solvation capacity for most of the aromatic acids and long chain aliphatic acids above palmitic.

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[1] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] Presented in part at the Spring Meeting of the American Chemical Society, St. Louis, Mo., March 27, 1961. Paper VIII is *J. Am. Chem. Soc.*, **81**, 3244 (1959).

[3] D. Swern, *Chem. Revs.*, **45**, 1 (1949).

[4] J. D'Ans and W. Frey, *Z. anorg. Chem.*, **84**, 145 (1914).

[5] B. Phillips, P. S. Starcher, and B. D. Ash, *J. Org. Chem.*, **23**, 1823 (1958).

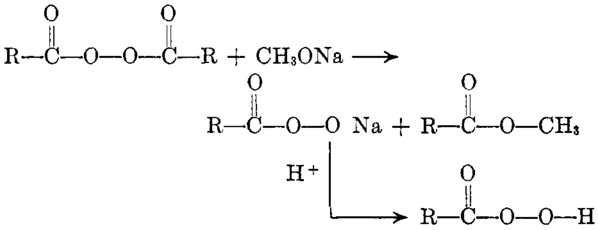
[6] W. E. Parker, C. Ricciuti, C. L. Ogg, and D. Swern, *J. Am. Chem. Soc.*, **77**, 4037 (1955).

[7] W. E. Parker, L. P. Witnauer, and D. Swern, *J. Am. Chem. Soc.*, **79**, 1929 (1957).

[8] M. Vilkas, *Bull. soc. chim. France*, **1959**, 1401, attempted to prepare *p*-nitroperoxybenzoic acid by this direct method and also failed.

Peroxy acid synthesis by basic perhydrolysis of acyl chlorides at low temperatures gives good yields (above 85%) of peroxy acids only for acid chlorides of relatively strong acids, such as α,α-dichlorolauroyl chloride, *p*-nitrobenzoyl chloride, and benzoyl chloride.[8] Acid chlorides of weaker acids, such as lauroyl chloride and α-chlorolauroyl chloride, give 30% and 61% yields of the respective peroxy acids, thereby showing some of the limitations of this method. The acyl chloride perhydrolysis method is better suited instead for the preparation of diacyl and diaroyl peroxides although it may be usefully applied to the preparation of those peroxy acids which are derived from strong parent acids or which have sufficiently low solubilities to precipitate from solution as they form before further acylation to diacyl or diaroyl peroxides can occur.

Basic hydrolysis of diacyl and diaroyl peroxides might be considered to be a general method,[3,9–11] but yields of peroxy acids are low, as only 50% of the aroyl or acyl groups is available for peroxy acid formation and 50% is lost by ester formation as shown in the equation below:



$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R + CH_3ONa \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-O\ Na + R-\overset{O}{\overset{\|}{C}}-O-CH_3$$

$$\xrightarrow{H^+} R-\overset{O}{\overset{\|}{C}}-O-O-H$$

Over-all peroxy acid yields are even lower when based on the parent acid, since additional steps are required to obtain the necessary peroxide: acid→acyl chloride→diacyl peroxide.

We wished to develop a general procedure for the direct preparation of aromatic and aliphatic peroxy acids including those containing acid-labile groups. Because formation of aliphatic peroxy acids is rapidly accelerated in concentrated sulfuric acid in accordance with the equations[6] it appeared

$$RCO_2H + H_2SO_4 \rightleftarrows RCO_2H_2^+ + HSO_4^- \qquad (1)$$

$$RCO_2H_2^+ + H_2O_2 \rightleftarrows RCO_3H + H_3O^+ \qquad (2)$$

reasonable to replace sulfuric acid by an acid of comparable strength and of lower oxidation and higher solvation capacity.

We have now found methanesulfonic acid to be most useful for this purpose. It has a $pK \simeq 0$[12] and shows good solvent capacity for many carboxylic acids at and above room temperature. Most of the resulting peroxy acids precipitate from the medium as they form, thus facilitating isolation and recovery. The use of 90–95% hydrogen peroxide in this variation has the further advantage of driving the equilibrium to high conversions by minimizing the water content. Although lower strength hydrogen peroxide can also be used, conversion of carboxylic acid to peroxy acid is lower (see Experimental).

EXPERIMENTAL

Materials. Hydrogen peroxide (50% and 98%) was supplied by BECCO Chemical Division of Food Machinery and Chemical Corp.[13] The hydrogen peroxide concentration slowly decreased from 98 to 94% during the course of this study. Hydrogen peroxide of 70% concentration was prepared from the 94% strength by dilution.

Methanesulfonic acid (Eastman Chemicals, Practical Grade) was used without further purification for the bulk of this study. A distilled sample (148–154°/0.5 mm., 99% purity) offered no advantage over the undistilled reagent when applied to *p-tert*-butylperoxybenzoic acid. Ethanesulfonic acid was Eastman White Label Grade.

The following carboxylic acids were used: *p*-methoxybenzoic, *o*-nitrobenzoic, *p*-nitrobenzoic, sebacic (Eastman White Label); *m*-methoxybenzoic (K. and K. Laboratories, Inc.); *p-tert*-butylbenzoic (recrystallized from ethyl ether; Shell Chemical Co.); α-bromostearic (prepared by G. Sasin, Drexel Institute of Technology); α-bromocapric (Columbia Organic Chemicals); 12-hydroxystearic (prepared by H. B. Knight, this laboratory); benzoic (Mallinckrodt AR); terephthalic (technical grade from E. I. du Pont de Nemours & Co.); *p*-cyanobenzoic (Aldrich Chemical Co., Inc.); methyl palmitate, stearic and lauric acids were purified as previously described.[14] Dimethyl terephthalate was a Du Pont refined grade.

NOTE: All preparations of peroxy acids described in this paper were carried out in open beakers behind a safety shield.

Attempted use of sulfuric acid for preparation of aromatic peroxy acids. The method described for preparing long chain aliphatic peroxy acids[6] was applied to several aromatic acids. Benzoic acid carbonized on addition of the hydrogen peroxide. Addition of hydrogen peroxide to a sulfuric acid solution of *p-tert*-butylbenzoic acid produced a dark brown viscous solution accompanied by a rapid temperature rise. *o*-Nitrobenzoic and *p*-nitrobenzoic acids gave red-orange and yellow products, respectively. *p*-Methoxybenzoic acid formed a light green slurry in sulfuric acid and a brown mixture on addition of hydrogen peroxide. No peroxy acids were isolated in any of these cases.

Peroxybenzoic acid. Hydrogen peroxide (70%, 2.2 g. or 94%, 1.6 g.; 0.045 mole) was added dropwise in 10–15 min. with stirring to a slurry or partial solution of benzoic acid (3.7 g., 0.03 mole) in methanesulfonic acid (14.4 g., 0.15 mole) in an open tall-form beaker, maintaining the temperature at 20–30°. The reaction was exothermic during hydrogen peroxide addition. Benzoic acid completely dissolved during this period. A total of 2 hr. using 70% hydrogen peroxide or 1 hr. using 94% hydrogen peroxide was sufficient for quantitative reaction. The reaction mixture was cooled below 10° in an ice bath, chopped ice (10 g.) was cautiously added (*exothermic*) followed by addition of ice cold saturated ammonium sulfate solution (10 ml.), maintaining the temperature below 25°. Peroxybenzoic acid was extracted in a separatory funnel with three 20-ml. portions

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[9] C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4250 (1953).

[10] I. M. Kolthoff, T. S. Lee, and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).

[11] G. Braun, *Org. Syntheses*, **Coll. Vol. I**, 431 (1941).

[12] R. P. Bell, *The Proton in Chemistry*, Cornell University Press, Ithaca, N. Y., 1959, p. 99.

[13] Reference to commercial products is not intended to be a recommendation of these products by the U. S. Department of Agriculture over others not mentioned.

[14] D. Swern and E. F. Jordan, Jr., *J. Am. Chem Soc.*, **70**, 2334 (1948).

of benzene. The combined benzene extracts were washed with two 10-ml. portions of cold saturated ammonium sulfate solutions to ensure complete removal of traces of methanesulfonic acid and hydrogen peroxide, dried over anhydrous sodium sulfate, filtered and evaporated at 30° in a rotatory evaporator or evaporating dish in the hood under a stream of nitrogen to yield a colorless to light yellow viscous liquid. Complete evaporation should be conducted within a few hours as peroxybenzoic acid decomposes at the approximate rate of 2.5% per day (see Table III).

Conversions of benzoic to peroxybenzoic acid, as determined by aliquot sampling of the washed benzene solutions, were approximately 90% using a 50% molar excess of either 70% or 94% hydrogen peroxide. With a 100–200% molar excess of 94% hydrogen peroxide conversions were essentially quantitative. Owing to its volatility, some loss of peroxybenzoic acid occurred during benzene evaporation; over-all recovery of solid peroxy acid ranged from 70–90%. The washed benzene solution may be used directly in epoxidation or other oxidation studies without further isolation.

Peroxybenzoic acid crystallized at −20° in 65% yield from an olefin-free petroleum ether (b.p. 35–50°)-ethyl ether co-solvent (3:1) in a ratio of 4.5 ml./g. of peroxy acid. It crystallized in long white needles, m.p. 41.3–42.0°, after seeding the solution at about 5° before further cooling. Pure peroxybenzoic acid appeared to be obtainable in good yield by crystallization only when the crude product contained above 90% peroxy acid.

The reaction was repeated on a scale ten times that just described using the methanesulfonic acid to benzoic acid ratio of 3:1 with substantially identical results.[14a]

p-Nitroperoxybenzoic acid. This preparation of *p*-nitroperoxybenzoic acid is a general procedure for the majority of water-insoluble peroxy acids.

TABLE I

EFFECT OF SEVERAL VARIABLES ON PEROXYBENZOIC ACID FORMATION[a]

Time, Hr.	Hydrogen Peroxide Initial concn., %	Hydrogen Peroxide Mole % excess	% Conversion[b] 20°	% Conversion[b] 30°
1	50	50	34	75
3	50	50	66[c]	76
1	70	50		87
2	70	50	89	86[d]
1	94	50	87	92
1	94	100		92
1	94	200	94[d]	95[d]

[a] Methanesulfonic acid: benzoic acid = 5:1. [b] Peroxybenzoic acid determined iodometrically on aliquots of benzene solutions from which hydrogen peroxide was removed as described under Experimental. [c] 74% in 5 hr.; 78% in 7 hr. [d] Similar conversions were also obtained with methanesulfonic acid:benzoic acid mole ratio of 3:1.

Hydrogen peroxide (94%, 3.3 g., 0.09 mole) was added dropwise with stirring to a slurry of *p*-nitrobenzoic acid (5.0 g., 0.03 mole) in methanesulfonic acid (14.4 g., 0.15 mole) in an open tall-form beaker, maintaining the temperature of reaction at 40°. Complete addition of hydrogen peroxide required 10 min. The slurry thickened as peroxy acid precipitated. After a total reaction time of 3 hr., the mixture was cooled to 10–15°, and crushed ice (10 g.) was added, followed by cautious addition of ice cold water, maintaining the temperature below 25°. The mixture was filtered on a Buchner funnel, and the precipitate was washed with cold water several times and dried in a desiccator. *p*-Nitroperoxybenzoic acid of 99% purity was obtained in 94% yield. The peroxy acid was crystallized from chloroform (2 g. per 100 ml.) after dissolving the crude at 50°, seeding the solution, and progressively cooling to −20°. Analytically pure *p*-nitroperoxybenzoic acid was obtained in 70% yield.

Table I summarizes the work on preparation of peroxybenzoic acid.

Other peroxy acids (aromatic and aliphatic). Table II. The other peroxy acids listed in Table II were prepared by the procedure just described for *p*-nitroperoxybenzoic acid, with the quantities of reactants and reaction conditions as follows (recrystallizing solvent, solvent to compound ratio, recrystallization temperature, and per cent yields on recrystallization in parentheses).

TABLE II

PREFERRED EXPERIMENTAL CONDITIONS AND YIELDS OF PEROXY ACIDS OBTAINED

Peroxy Acids	Mole Ratio MSA: H_2O_2[a]:CA	Temp.	Time, Hr.	Peroxy Acid in Crude Product, %	Yield %[b]
	Aromatic				
Peroxybenzoic	5:1.5:1	20	1	93	87[c]
	5:3:1	20	1	100	94[c]
	5:1.5[d]:1	20	2	93	89[c]
p-*t*-Butylperoxybenzoic	5:3:1	40	3	98	86
p-Nitroperoxybenzoic	5:3:1	40	3	99	94
o-Nitroperoxybenzoic	5:3:1	60	1	99	76
Diperoxyterephthalic					
From terephthalic acid	10:6:1	60	2	20	
From dimethyl ester	20:6:1	50	2	93	93
p-Cyanoperoxybenzoic	8:3:1	40	1	95	75
	Aliphatic				
Peroxylauric	5:3:1	40	1	99	97
Peroxystearic	8:3:1	60	2	98	90
Peroxypalmitic from methyl ester	8:3:1	50	1.5	99	98
Diperoxysebacic	5:6:1	50	1	95	92
12-Hydroxyperoxystearic	5:3:1	30	1	94	90
α-Bromoperoxystearic	5:3:1	50	1	95	86
α-Bromoperoxycapric	5:3:1	40	1	97	85

[a] MSA = methanesulfonic acid, CA = carboxylic acid. Hydrogen peroxide concentration, 94% except where indicated. [b] Calculated by multiplying the purity of the crude product by the percentage yield. [c] Yield determined by iodometric analysis on the benzene solution before isolation of the peroxybenzoic acid. [d] Hydrogen peroxide concentration, 70%.

p-tert-Butylperoxybenzoic acid. Five and three-tenths grams (0.03 mole) of *p-tert*-butylbenzoic acid, 3.3 g. (0.09 mole) of 94% hydrogen peroxide and 14.4 g. (0.15 mole) of

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[14a] The large scale procedure will be reported in a forthcoming volume of *Organic Syntheses*.

methane sulfonic acid (petroleum ether–ethyl ether (2:1), 4.5 ml./g., −20°, 55%) were used.

o-Nitroperoxybenzoic acid. Five grams (0.03 mole) of o-nitrobenzoic acid, 3.3 g. (0.09 mole) of 94% hydrogen peroxide and 14.4 g. (0.15 mole) of methanesulfonic acid (warm chloroform, 28 ml./g., −20°, 58%) were used. [Note: To obtain uniform results in yield and purity of o-nitroperoxybenzoic acid, the reaction was terminated by pouring the methanesulfonic acid mixture into cold water saturated with ammonium sulfate, followed by water-washing the precipitate several times.]

Diperoxyterephthalic acid. Two and three-tenths grams (0.012 mole) of dimethyl terephthalate, 2.6 g. (0.072 mole) of 94% hydrogen peroxide and 11.6 g. (0.24 mole) of methanesulfonic acid were used. (Product was difficult to recrystallize from the usual solvents; further purification was not attempted).

p-Cyanoperoxybenzoic acid. Two and nine-tenths grams (0.02 mole) of p-cyanobenzoic acid, 2.2 g. (0.06 mole) of 94% hydrogen peroxide and 15.4 g. (0.16 mole) of methanesulfonic acid were used. (Product was difficult to recrystallize from the usual solvents; further purification was not attempted).

Peroxylauric acid. Three grams (0.015 mole) of lauric acid, 1.6 g. (0.045 mole) of 94% hydrogen peroxide and 7.2 g. (0.075 mole of methanesulfonic acid (petroleum ether, 10 ml./g., 0°, 65%) were used.

Peroxypalmitic acid. Forty and five-tenths grams (0.15 mole) of methyl palmitate, 16.5 g. (0.45 mole) of 94% hydrogen peroxide and 115.3 g. (1.2 mole) of methanesulfonic acid (petroleum ether, 15 ml./g., 0°, 89%) were used.

Peroxystearic acid. Stearic acid, 4.3 g. (0.015 mole), 1.7 g. (0.045 mole) of 94% hydrogen peroxide and 11.5 g. (0.12 mole) of methanesulfonic acid (petroleum ether, 20 ml./g., 0°, 91%) were used.

Diperoxysebacic acid. Three grams (0.015 mole) of sebacic acid, 3.3 g. (0.09 mole) of 94% hydrogen peroxide and 7.2 g. (0.075 mole) of methanesulfonic acid (chloroform at 50°, 40 ml./g., 0°, 70%) were used.

12-Hydroxyperoxystearic acid. 12-Hydroxystearic acid, 4.5 g. (0.015 mole), 1.7 g. (0.045 mole) of 94% hydrogen peroxide, and 7.2 g. (0.075 mole) of methanesulfonic acid (acetone, 2 ml./g., 0°, 62%) were used.

α-Bromoperoxy acids. Peroxy acids from α-bromocapric and α-bromostearic acids were prepared as described for peroxybenzoic acid. The peroxy acids, after water-quenching to terminate the reaction, are extracted with olefin-free petroleum ether instead of benzene. Quantities of reactants are as follows:

α-Bromoperoxycapric acid. Five grams (0.02 mole) of α-bromocapric acid, 2.2 g. (0.06 mole) of 94% hydrogen peroxide, and 9.6 g. (0.10 mole) of methanesulfonic acid were used.

α-Bromoperoxystearic acids. α-Bromostearic acid, 5.4 g. (0.015 mole), 1.7 g. (0.045 mole) of 94% hydrogen peroxide and 7.2 g. (0.075 mole) of methanesulfonic acid were used. α-Bromoperoxycapric acid, a liquid, was not further purified Pure α-bromoperoxystearic acid crystallized from petroleum ether, 10 ml./g., at −20° in 72% yield.

Ethanesulfonic acid as solvent and reaction medium. Some preliminary studies with ethanesulfonic acid as a solvent-catalyst for preparation of peroxystearic and p-nitroperoxybenzoic acids were undertaken with the view that increased solubilities of the carboxylic acids and lower reaction temperatures might be obtained. With an ethanesulfonic acid to stearic acid mole ratio of 7, only 50% (30°, 3 hr. reaction) and 72% (40°, 2–5 hr. reaction) of peroxy acid were obtained. With an ethanesulfonic acid to p-nitrobenzoic acid mole ratio of 4, only 20% of peroxy acid (30°, 1 hr. reaction) was obtained. No attempt was made to find optimum reaction conditions; further work with ethanesulfonic acid was discontinued.

Analytical. I. *Iodometric.* Peroxy acids were analyzed by an iodometric method,[15] in which potassium iodide was replaced by sodium iodide. With insoluble peroxy acids, such as diperoxyterephthalic acid, the method was modified by replacing chloroform with acetone. With diperoxysebacic acid, aqueous acetic acid was used.[7]

Conversions of benzoic acid to peroxybenzoic acid were determined by iodometric analysis of aliquots of the washed benzene solutions. Absence of hydrogen peroxide was confirmed by a modified ceric sulfate–iodometric method.[16]

The conversions in Table I should be increased by approximately 5%, a factor that represents peroxybenzoic acid loss due either to incomplete benzene extraction or to its re-extraction from the combined benzene extracts by a final water-wash performed to ensure complete removal of any residual hydrogen peroxide and methanesulfonic acid. This view is supported by the observation that peroxybenzoic acid samples isolated by evaporation of benzene are in some cases almost 100% pure when 94% strength of hydrogen peroxide was used. Because actual yields (70–90%) of recovered peroxy acid are lower than the solution values owing to volatilization of peroxybenzoic acid, the solution analyses are a more accurate and reliable measure for determining the conversions.

II. *Proof of structure of selected peroxy acids. p-Cyanoperoxybenzoic acid.* Peroxy acid content of the isolated crude product was 95% of the calculated value.

Anal. Calcd.: N, 8.59. Found: N, 8.08.

The product isolated from the iodometric analysis of the peroxy acid had a m.p. of 215–217° (melting point of authentic p-cyanobenzoic was 217°) and nitrogen content 9.18% (calculated for p-cyanobenzoic acid 9.57%). A mixed melting point with p-cyanobenzoic acid was 214.5–216.5°. This evidence supports the conclusion that the cyano group remains unaltered during peroxy acid formation

α-Bromoperoxystearic acid. Peroxy acid content of the crude product was 95% of the calculated value.

Anal. Calcd.: Br, 21.1. Found: Br, 19.9.

The product isolated from the iodometric analysis proved to be α-bromostearic acid.

Anal. Calcd. for Br, 22.0; acid no., 154.4. Found: Br, 21.6; acid no., 156.7.

12-Hydroperoxystearic acid. 12-Hydroxystearic acid dissolves in methanesulfonic acid to form a light brown solution suggesting possible structural alteration. Further structural analysis is required to check also the possible formation of dihydroxyperoxystearic acid or isomeric monohydroxyperoxystearic acids which could arise by acid catalyzed dehydration followed by epoxidation and hydrolysis or acid-catalyzed rehydration, respectively. The crude hydroxyperoxystearic acid (purity 94%) was recrystallized from acetone and was obtained in 98.6% purity (calculated as a monohydroxyperoxystearic acid) as determined iodometrically. The reduced product recovered from the iodometric analysis had an acid number of 184.4; calculated for monohydroxystearic acid, 186.7.

The x-ray diffraction pattern of the monohydroxystearic acid recovered from the iodometric analysis was compared

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(15) (a) D. H. Wheeler, *Oil & Soap*, **9**, 89 (1932); (b) D. Swern, *Org. Reactions*, **VII**, 392 (1953).

(16) The differential hydrogen peroxide–peroxy acid method of F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20**, 1061 (1948) is satisfactory for water-soluble peroxy acids but inadequate for water-insoluble peroxy acids and their nonaqueous solutions. Large quantities of water and the presence of chloroform or hydrocarbon solvents diminish the rate of iodine liberated between peroxyacid and iodide. The following modifications to the procedure gave satisfactory results on known test solutions of peroxy acid–hydrogen peroxide mixtures: (i) vigorous magnetic stirring during the entire analysis; (ii) substitution of 20 ml of 10% sulfuric acid for the 150 ml. of 5% sulfuric acid; (iii) substitution of solid potassium iodide (3 g.) for aqueous potassium iodide; (iv) allowing 20 min. for complete liberation of iodine.

TABLE III

PROPERTIES OF PEROXY ACIDS

Peroxy Acid	M.P.	Δ M.P.[a]	% Peroxide Oxygen Found	% Peroxide Oxygen Calcd.	Stability,[b] % Weeks 2	4	8
		New					
p-t-Butylperoxybenzoic	81.5–83	80	8.21	8.24	100	99.4	99.2
o-Nitroperoxybenzoic	95–96[c]	52	8.70	8.74	100	99.3	98.6
p-Cyanoperoxybenzoic	126–128	92	9.32	9.81			
α-Bromoperoxystearic	41–42	18	4.22	4.22	43[d]	16	<1
12-Hydroxyperoxystearic	62–64	17	4.99	5.06			
Peroxystearic	65–65.5	5	5.34	5.32			
		Previously Prepared					
Peroxybenzoic	41.3–42[e]	80	11.53	11.59	63[f]	34	2.5
p-Nitroperoxybenzoic	138[g] dec.	103	8.71	8.74	100	100	100
Diperoxyterephthalic			15.02	16.15	99.7[h]	96.3	95.1
Peroxylauric	50–50.5[i]	−7	7.41	7.40	99.4	97.7	95.9
Diperoxysebacic	93.2–94	41	13.65	13.61			
Peroxypalmitic	60.3–60.8[j]	3	5.92	5.87			

[a] Melting point difference between parent acid and peroxy acid. Negative sign indicates a lower melting point for the parent acid. [b] Per cent of peroxy acid retained on storage of solid compound at 25°. Initial purity of all peroxy acids is 100% except diperoxyterephthalic acid (see *h* below). [c] Determined in capillary tube in a bath preheated to 85° before capillary immersion; m.p. 91–93° in sealed capillary tube by normal method of slow, progressive heating. [d] One week, 63%. [e] Baeyer and Villiger, *Ber.*, **33**, 1569 (1900), report m.p. 41–43°; Fischer *et al.*, *Ann.*, **486**, 80 (1931), report m.p. 39–40°; ref. 9 reports m.p. 40–41.5°. [f] One week, 81%; six weeks, 11%. [g] Decomposes at this temperature in a sealed capillary tube on immersion in a bath preheated to 132° and using a heating rate of 4° per minute. Ref. 9 reports m.p. 134–136°. [h] Initial purity, 93%; stability values represent the per cent of initial peroxyterephthalic acid remaining undecomposed. [i] Ref. 6 reports m.p. 52°. [j] Ref. 6 reports m.p. 61–61.5°.

with that of authentic 12-hydroxystearic acid, after both were crystallized from acetone by slow evaporation of solvent. The x-ray patterns were nearly identical in all respects; they differed only in the relative intensities of two major peaks. The pattern for 12-hydroxystearic acid distinctly differs from that for 10-hydroxystearic acid (11-isomer was not available for study). The conclusion is that both the authentic and the isolated samples consisted of two polymorphs which differed only in their relative amounts. This is a physical difference, not a chemical (isomeric) one for the monohydroxystearic acid. The hydroxyl group, therefore, appears to be retained with little, if any, isomerization occurring during formation of the peroxy acid.

Melting points. Melting points of peroxy acids were determined in a Thomas-Hoover "Uni-Melt" capillary melting point apparatus. Capillary samples were immersed in the bath at 5–10° below their melting point, approximately determined on preliminary samples, with the bath temperature increasing at a rate of 1–2° per minute for the final measurement.

Stability studies. Peroxy acids stored at room temperature (25° ± 2°) were periodically analyzed by iodometry for their remaining peroxide content. The stability data are reported in Table III as per cent peroxy acid remaining after storage for 2, 4, and 8 weeks at 25°.

Solid α-bromoperoxystearic acid decomposed at 25° to α-bromostearic acid.

Anal. Calcd.: Br, 22.0; acid no., 154.4. Found: Br, 20.7, acid no., 154.3.

Solid peroxybenzoic acid decomposes at 25° to benzoic acid.

Anal. Calcd.: acid no., 459. Found: acid no., 461.

DISCUSSION

The effects of the variables–hydrogen peroxide concentration, molar excess of hydrogen peroxide, time, temperature, and ratio of methanesulfonic acid to carboxylic acid on the conversion of benzoic acid to peroxybenzoic acid were studied for determination of the optimum conditions. Table I summarizes the results.

Benzoic acid dissolves readily in methanesulfonic acid when the methanesulfonic acid:carboxylic acid mole ratio is above 3. With hydrogen peroxide strengths above 70%, the optimum temperature range for reaction is 20–30° with less side oxidation and decomposition occurring at the lower temperature. A 50% molar excess of hydrogen peroxide is sufficient for nearly quantitative conversion to peroxy benzoic acid, although quantitative conversion is attainable only with the 90% or higher strength in above 50% molar excess. Hydrogen peroxide of 50% strength gives conversions of only 75% in one hour at 30° and in seven hours at 20°.

Similar results were obtained for *p*-nitroperoxybenzoic and *p-tert*-butylbenzoic acids. A slightly higher temperature was required for dissolving the carboxylic acid in the reaction medium. The peroxy acids precipitated to form pasty mixtures as reaction proceeded but at the optimum reaction temperature, these mixtures were sufficiently fluid to permit easy stirring. The results obtained indicate that by use of 90–95% hydrogen peroxide in 200% molar excess, with sufficient methanesulfonic acid as solvent-catalyst, and by judicious choice of reaction temperature, many carboxylic acids of varied structure and size may be converted to their peroxy acids in excellent yield.

The methanesulfonic acid technique was applied to a representative group of carboxylic acids to determine its general applicability. Table II summarizes the preferred experimental conditions to give high (often quantitative) yields of crude reaction products having high peroxy acid content. The isolated product in most cases was nearly pure peroxy acid.

In the aromatic series with the exception of peroxybenzoic acid high conversions to peroxy acids were obtained only when 90% or higher strength hydrogen peroxide was used. The methanesulfonic acid:carboxylic acid mole ratio of 5 was adequate for most of the compounds studied, but higher ratios were necessary in a few cases as shown in Table II, owing to low solubility of the carboxylic acid or tendency of the precipitating peroxy acid to form a paste with the undissolved acid before reaction was complete. Temperatures of 30–40° were optimum in most cases but higher temperatures and higher methanesulfonic acid:carboxylic acid mole ratios were necessary for those acids of very low solubility or high melting point (intermolecular hydrogen bonding). The low conversion of terephthalic acid to peroxy acid, for example, was probably a function of both effects. Replacement of terephthalic acid by its dimethyl ester, which dissolves readily in methanesulfonic acid at 50°, overcame solubility difficulties to permit high peroxy acid conversions. Preparation of peroxystearic acid in high yields and purity is another striking example of the applicability of the present method. This compound could not be obtained in pure form by the sulfuric acid method previously reported.[6]

o-Nitrobenzoic acid required a high reaction temperature than its *p*-isomer for effective conversion to peroxy acid. A lower yield (76%) resulted owing to acid-catalyzed decomposition of the *ortho* peroxy acid at the higher temperature (60°) as evidenced by a nitrobenzene odor which usually attended its preparation. The methyl ester should permit a lower operating temperature and less decomposition, but this was not studied.

Parent carboxylic acids of 12-hydroxyperoxystearic, α-bromoperoxystearic and *p*-cyanoperoxybenzoic acids were isolated as primary products from their iodometric analyses, thus demonstrating little, if any, attack on or removal of the hydroxyl, bromo, and cyano groups during peroxy acid formation even though some color change was noted during reactions.

Attempts to prepare the corresponding peroxy acids from *p*- and *m*-methoxybenzoic acids by this method were unsuccessful. The reaction mixtures, highly exothermic during hydrogen peroxide addition, turned dark brown during the reactions and the isolated products contained no peroxide oxygen.

Decomposition data for some peroxy acids in the solid, liquid and solution states have been reported[3,10,17,18] but little information is available on rates of decomposition of solid peroxy acids at 25°. This information is of utility for room temperature storage of the more stable peroxy acids in either a pure state or in formulations where thermal stability is desired. A true kinetic evaluation was not attempted, but rather the periodic room temperature decompositions were recorded (Table III). (The time required for 50% decomposition to occur would be a preferred characterization of stability, but the slow decomposition of the more stable peroxy acids made such an evaluation impractical).

p-Nitroperoxybenzoic acid, the most stable of all the peroxy acids examined, showed no decomposition during the test period. Peroxybenzoic acid was very much less stable than any of its substituted derivatives. Its low stability may be attributed to its low melting point (41°); hence, sufficient kinetic energy is available at room temperature for a significant decomposition rate to occur. The dependence of peroxide stability on the phase state is evident also in the stability of solid long-chain diacyl peroxides, such as dilauroyl peroxide (m.p. 55°), which showed no decomposition at room temperature after eighteen months, whereas liquid dipelargonyl peroxide (m.p. 13°) lost 80% of its peroxide oxygen in seven months and 98% in eighteen months at 25°.[19]

α-Substitution in aliphatic peroxy acids lowers the stability, as illustrated by α-bromoperoxystearic acid. This may also be due to the low melting point (41°), although the inductive effect of bromine may contribute to lowering stability by reducing the capacity for intramolecular hydrogen bonding in the peroxycarboxyl group through a reduction of the electron density of the carbonyl group.

Peroxybenzoic and α-bromoperoxystearic acids in their solid states each decomposed at room temperature to their parent acids.

Melting points of the parent carboxylic acids are higher than those of the corresponding peroxy acids in nearly all cases. The melting point difference between parent acid and peroxy acid is recorded in Table III as ΔM.P. In the aromatic series the parent carboxylic acids melt 50–100° higher. A similar relationship exists only in part in the aliphatic series and with smaller melting point differences. The ΔM.P. for the sebacic pair is twice that for the substituted stearic pairs, presumably because of its dibasic character by which each peroxycarboxyl group contributes equally to lowering the melting point.

The lower melting points of aromatic peroxy acids are attributed to intramolecular-hydrogen bonding (monomeric, five-membered ring) as

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(17) W. E. Parker, L. P. Witnauer, and D. Swern, *J. Am. Chem. Soc.*, **80**, 323 (1958).

(18) S. R. Cohen and J. O. Edwards, *J. Phys. Chem.*, **64**, 1086 (1960).

(19) Unpublished results from this laboratory.

distinguished from intermolecular-hydrogen bonding (dimeric, eight-membered ring) present in the parent acids. The peroxycarboxyl group containing the additional electronegative oxygen should have a larger polarity that might have more of an effect in raising the melting point that the corresponding carboxyl group. In contrast, the dimeric eight-membered carboxylic acid ring, which is nearly planar, should permit a closer packing arrangement than that permitted by the five-membered, skewed ring of the peroxy acid. A closer packing arrangement would permit a stronger influence of van der Waals' forces.

The molecules in benzoic acid occur as nearly planar, centrosymmetric dimers, with hydrogen bonds between the adjacent carboxyl groups.[20] The crystal structure of peroxybenzoic acid (or any other peroxy acid) is still to be determined but a dihedral angle of 72° for the monomeric, five-membered peroxy acid ring was derived by electric moment studies.[21] The skew resulting from this dihedral angle indicates a less dense packing arrangement to be present in peroxybenzoic acid; hence, lower van der Waals' attractions of the phenyl rings. This effect should reflect in a lower melting point, which does occur to the extent of 80° in the benzoic-peroxybenzoic system, with a similar effect noted with the substituted benzoic derivatives.

In the aliphatic series, in contrast, peroxy acids have higher melting points than the carboxylic acids up to and including C-14. With C-16, the melting point curves cross, and palmitic acid (m.p. 63°) has a higher melting point than peroxypalmitic acid (m.p. 61°). As explained for the aromatic acids, the near planarity of dimeric carboxylic acid groups should also permit a more closely packed arrangement relative to that for the skewed ring of the peroxy acids.[22] For the shorter aliphatic chains, however, the higher polarity of the peroxycarboxyl is sufficiently dominant to exert a more positive effect on melting point than the weaker van der Waals' interactions. As chain length increases, terminal polar effects diminish relative to the increased van der Waals' attractions

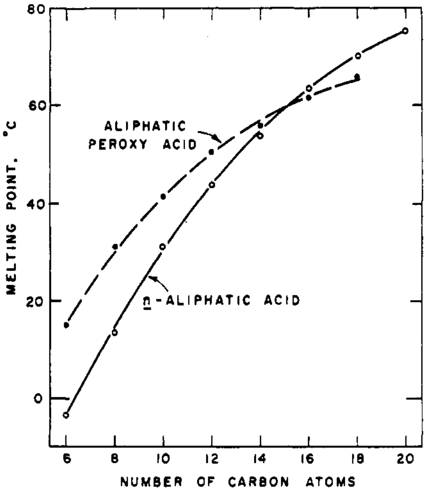

Fig. 1. Peroxides IX

As shown in Fig. 1, the relative rate of change of the melting points with increasing number of carbon atoms is greater with acids than with peroxy acids, as reflected in the steeper slope, presumably due to the closer packing arrangement that permits a stronger van der Waals' effect compared to that in peroxy acids. The melting point curves will eventually cross with the acids then having the higher melting points, as was observed for the aromatic pairs.

The much larger melting point difference observed for aromatic acid–peroxy acid pairs than for aliphatic pairs can be explained in terms of the larger van der Waals' forces exerted by phenyl rings than by aliphatic chains. The peroxy acid skew offsets copolanarity of the phenyl rings with a large attendant reduction in attraction forces. The lowering of these forces is considerably less for the aliphatic carboxylic acid–peroxy acid pairs, as free rotation in the chains permits a larger number of possible orientations with a close similarity of chain alignment.

Methanesulfonic acid has subsequently been shown to be an effective solvent-catalyst in other reactions in which sulfuric acid is unsatisfactory. Forthcoming reports will describe this work.[23]

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(21) (a) W. Lobunez, J. R. Rittenhouse, and J. G. Miller, *J. Am. Chem. Soc.*, **80**, 3505 (1958). (b) J. R. Rittenhouse, W. Lobunez, D. Swern, and J. G. Miller, *J. Am. Chem. Soc.*, **80**, 4850 (1958).

(22) In an earlier publication, *J. Am. Chem. Soc.*, **77**, 5537 (1955), it was reported that aliphatic peroxy acids and the *C*-form of *n*-aliphatic acids crystallize in bimolecular layers with the same angle of tilt.

(23) For example, see A. Eisner, T. Perlstein, and W. C. Ault, Paper presented at American Oil Chemists' Society Meeting, Chicago, Ill., Oct. 30–Nov. 1, 1961, and W. C. Ault and A. Eisner, *J. Am. Oil Chemists' Soc.*, **39**, 132 (1962).