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# Peroxides. II. Preparation, Characterization and Polarographic Behavior of Long-chain Aliphatic Peracids[2]

By Winfred E. Parker, Constantine Ricciuti, C. L. Ogg and Daniel Swern

A new procedure for the preparation of aliphatic peracids is described. This consists in the reaction of fatty acids with 0.5–2.0 moles of 50–65% hydrogen peroxide in concentrated sulfuric acid solution. The reaction is an excellent example of the nucleophilic character of hydrogen peroxide. Yields of $C_6$- to $C_{18}$-peracids range from 61–99%, the reactions are rapid at 10 to 30° and product isolation is readily accomplished. The $C_7$- to $C_{-18}$-peracids are new compounds and, with the exception of perstearic acid, have been characterized by melting point, ultimate analysis, and chemical and polarographic behavior. Kinetics of decomposition of eight peracids in methanol–benzene have been determined. Pseudo-first order specific reaction rate constants at 25° range from 0.93 to $1.92 \times 10^{-3}$ min.$^{-1}$ over the molar concentration range of $4–20 \times 10^{-3}$ mole/l.

Aliphatic peracids were first prepared and their properties examined by D'Ans and co-workers during the first two decades of the twentieth century,[3,4] although dilute aqueous solutions had probably been obtained somewhat earlier.[5–7] D'Ans and co-workers prepared concentrated performic, peracetic, perpropionic and perbutyric acids usually by the reaction of concentrated (up to 98%) hydrogen peroxide with the appropriate acid or anhydride in the presence of catalytic quantities of inorganic acids or acid salts. The products then were purified by distillation and fractional freezing. (It is noteworthy that the original melting and boiling points recently have been confirmed.[8])

With the exception of percaproic acid,[9] m.p. 15°, b.p. 61–62° (13 mm.) and 41–42° (0.5 mm.), the preparation of the remaining *n*-aliphatic peracids has not been described. Occasionally a passing reference can be found to water-insoluble aliphatic peracids,[4] such as perlauric,[10] perpal-

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(2) Presented at the Spring Meeting of the American Chemical Society, Cincinnati, Ohio, March 29–April 7, 1955. The previous paper in this series is in *Org. Syntheses*, **34**, 90 (1954).

(3) J. D'Ans, German Patent 228,665 (1910); J. D'Ans, German Patent 251,802 (1911); J. D'Ans, *Z. Elektrochem.*, **17**, 849 (1911); J. D'Ans and W. Frey, *Ber.*, **45**, 1845 (1912); J. D'Ans and W. Frey, *Z. anorg. Chem.*, **84**, 145 (1914); J. D'Ans and W. Friederich, *Ber.*, **43**, 1880 (1910); J. D'Ans and J. Friederich, German Patent 236,768 (1910); J. D'Ans and J. Friederich, *Z. anorg. Chem.*, **73**, 325 (1912); and J. D'Ans and A. Kneip, *Ber.*, **48**, 1136 (1915).

(4) D. Swern, *Chem. Rev.*, **45**, 1 (1949). Consult this article for other pertinent references.

(5) A. M. Clover and A. C. Houghton, *Am. Chem. J.*, **32**, 43 (1904); A. M. Clover and G. F. Richmond, *ibid.*, **29**, 179 (1903).

(6) P. C. Freer and F. G. Novy, *ibid.*, **27**, 161 (1902).

(7) Parke, Davis and Co., German Patent 156,998 (1902).

(8) A. C. Egerton, W. Emte and G. J. Minkoff, *Disc. Faraday Soc.*, **10**, 278 (1951).

(9) F. Fichter and R. Zumbrunn, *Helv. Chim. Acta*, **10**, 869 (1927).

(10) L. D. Small, J. H. Bailey and C. J. Cavallito, This Journal, **69**, 1710 (1947).

mitic[3] or perstearic acid,[11] but these compounds have not been isolated nor have their physical properties been reported.

The preparation of aliphatic peracids containing six or more carbon atoms presents certain difficulties. The low solubility of the parent acid in aqueous hydrogen peroxide prevents intimate contact between the reactants and causes the reaction to proceed at a low rate. The reaction of long-chain anhydrides[9] or mixed boric–acyl anhydrides[3,4] with aqueous hydrogen peroxide offers some promise but the requisite starting materials either are not readily available or are expensive. The reaction of acyl halides with hydrogen peroxide in a Schotten–Baumann reaction is better suited for the preparation of diacyl peroxides than of peracids.

Concentrated sulfuric acid is a good solvent for most aliphatic acids and also for 50–65% hydrogen peroxide. We have found that long-chain aliphatic peracids can be prepared directly from the parent carboxylic acids and 50–65% (usually 50%) hydrogen peroxide using 95% sulfuric acid as the cosolvent and reaction medium. Operating in this way, the relatively inexpensive and plentiful fatty acids, rather than anhydrides or acyl halides, can be used; the molar ratio of reactants is in the range of 1 (fatty acid) to 0.5–2.0 (hydrogen peroxide); the reactions are rapid at 10 to 30° and rarely require more than one hour reaction time; conversions to peracid are high and often quantitative; and the isolation of product is accomplished readily by dilution of the reaction mixture with cold water followed by filtration or extraction. Because of the low solubility of palmitic ($C_{16}$) and stearic ($C_{18}$) acids in sulfuric acid it is not practical to use sufficient sulfuric acid to dissolve them completely. In these cases only moderately high conversions (60–65%) to peracid are obtained; in all others conversions are 85–99%.

Sulfuric acid (70–95%) has been used as a reaction medium by Milas and co-workers in the preparation of some peroxides and hydroperoxides.[12] Its use in the preparation of aliphatic peracids has not been described previously, to the best of our knowledge.

## Experimental

**Starting Materials.**—Fifty per cent. hydrogen peroxide was obtained through the courtesy of Dr. Frank P. Greenspan of the Buffalo Electrochemical Co.; the 65% grade was obtained through the courtesy of Dr. John G. Wallace of E. I. du Pont de Nemours & Co.

The preparation of pure caproic, caprylic, pelargonic, capric, lauric, myristic, palmitic and stearic acids already has been described.[13] Hendecanoic acid, m.p. 28°, and tridecanoic acid, m.p. 40°, were Eastman Organic Chemicals.

**Perlauric Acid. Reaction of Lauric Acid with Hydrogen Peroxide.**[14]—The preferred procedure is given in detail. Twenty grams (0.1 mole) of lauric acid was dissolved in 43 g. of 95% sulfuric acid in a tall-form beaker and the straw-yellow solution was cooled to 10° in an ice-bath. With efficient agitation, 10.2 g. (0.15 mole, 50% excess) of 50% hydrogen peroxide then was added dropwise at such a rate that the temperature could be maintained easily between 20 and 30°. This required about 10 minutes. The reaction mixture was stirred for an additional 50 minutes (total reaction time, 1 hour), several volumes of ice and water were slowly added and the precipitated perlauric acid was extracted with ether. The ether solution was washed with water until free of sulfuric acid and $H_2O_2$ and then dried over anhydrous sodium sulfate. Filtration and evaporation of the ether yielded 19–22 g. of crude perlauric acid as a white solid; peroxide oxygen content, 7.15%[15] (calculated 7.40%). Its purity, therefore, was 97%. The conversion of lauric to perlauric acid was substantially quantitative; conversion of hydrogen peroxide to peracid was about 65%.

Crystallization of the crude perlauric acid (5 g.) from petroleum naphtha, boiling range 35–60° (10 ml./g. of solute) at 0° yielded analytically pure perlauric acid (3 g.) as long glistening needles, m.p. 52°; peroxide oxygen, 7.50%; carbon, 66.6 (calculated 66.7); hydrogen 11.0 (calculated 11.1).

With a 100% molar excess of 50% hydrogen peroxide, the crude perlauric acid weighed 22 g. and had a peroxide oxygen content of 7.23%. Its purity was 98%. Conversion of lauric acid was substantially quantitative; conversion of hydrogen peroxide was 49%. Total mixing and reaction time was only 30 minutes.

With a 5% molar excess of hydrogen peroxide and a total reaction time of 1 hour, the crude perlauric acid had a peroxide oxygen content of 6.02% (a 10-minute reaction time gave a peroxide oxygen content of only 4.92%). Its purity was 81%. Conversion of lauric acid was 81%; conversion of hydrogen peroxide was 77%.

With an excess of lauric acid (0.1 mole to 0.079 mole of 50% hydrogen peroxide), the crude perlauric acid had a peroxide oxygen content of 4.45%. Its purity was 60%. The conversion of lauric acid was 60%; conversion of hydrogen peroxide was 76%.

**Other Aliphatic Peracids.**—The other peracids listed in Table I were prepared by the first procedure under perlauric acid, with the quantities of reactants as follows (recrystallization temperature in parentheses). Percaproic acid: 23.2 g. (0.2 mole) of caproic acid, 46.4 g. of 95 or 100% $H_2SO_4$ and 20.4 g. (0.3 mole) of 50% hydrogen peroxide or 15.7 g. of 65% hydrogen peroxide (−30°). Percaprylic acid: 21.6 g. (0.15 mole) of caprylic acid, 32.4 g. of 95% sulfuric acid and 15.3 g. (0.225 mole) of 50% hydrogen peroxide (−20°). Perpelargonic acid: 23.7 g. (0.15 mole) of pelargonic acid, 39.2 g. of 95% sulfuric acid and 15.3 g. (0.225 mole) of 50% hydrogen peroxide (−20°). Percapric acid: 17.2 g. (0.1 mole) of capric acid, 30 g. of 95% sulfuric acid and 10.2 g. (0.15 mole) of 50% hydrogen peroxide (−20°). Perhendecanoic acid: 10.0 g. (0.054 mole) of hendecanoic acid, 20 g. of 95% sulfuric acid and 5.5 g. (0.08 mole) of 50% hydrogen peroxide (0°). Pertridecanoic acid: 10.0 g. (0.047 mole) of tridecanoic acid, 22 g. of 95% sulfuric acid and 5.1 g. (0.075 mole) of 50% hydrogen peroxide (0°). Permyristic acid: 22.8 g. (0.1 mole) of myristic acid, 60 g. of 95% sulfuric acid and 10.2 g. (0.15 mole) of 50% hydrogen peroxide (0°). Perpalmitic acid: 25.6 g. (0.1 mole) of palmitic acid, 77 g. of 95% sulfuric acid and 10.2 g. (0.15 mole) of 50% hydrogen peroxide (0°). Perstearic acid: 20 g. (0.07 mole) of stearic acid, 60 g. of 95% sulfuric acid and 7.2 g. (0.105 mole) of 50% hydrogen peroxide (product could not be purified by crystallization).

**Reduction of Perlauric Acid to Lauric Acid.**—The final solution obtained in the analysis of 0.207 g. (0.00096 mole) of pure perlauric acid for its peroxide oxygen content[15] was extracted with ether. The ether solution was washed several times with cold water to remove acetic acid and salts. Evaporation yielded 0.19 g. (99% yield) of pure lauric acid, m.p. 43.5–44° and neutralization equivalent 201 (calcd. 200). A mixed melting point with an authentic sample of lauric acid was unchanged.

**Epoxidation of Oleic Acid with Perpelargonic Acid.**—A solution was prepared consisting of 8.86 g. (0.0314 mole) of oleic acid (iodine number 88.5) and 6.0 g. (0.0345 mole) of perpelargonic acid in 30 ml. of benzene at 20–25°. After 4 hours, analysis[15] showed that peroxide consumption was complete. The benzene was evaporated and the residue (15 g.) was crystallized from petroleum naphtha at 5°. The insoluble white solid weighed 6.1 g. and consisted of

(11) J. D'Ans and J. Mattner, *Chem. Zeitung*, **74**, 435 (1950).

(12) N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205, 643 (1946); N. A. Milas and L. H. Perry, *ibid.*, **68**, 1938 (1946); N. A. Milas and O. L. Mageli, *ibid.*, **74**, 1471 (1952); **75**, 5970 (1953).

(13) D. Swern and E. F. Jordan, Jr., *ibid.*, **70**, 2334 (1948).

(14) All preparations of peracids described in this paper were carried out in open beakers behind a safety shield.

(15) D. H. Wheeler, *Oil and Soap*, **9**, 89 (1932).

TABLE I

$C_6$–$C_{18}$ ALIPHATIC PERACIDS

| Peracid | Conversion, % | M.p., °C. | Peroxide oxygen, % Calcd. | Peroxide oxygen, % Found | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|---|
| Percaproic | 87 | 15[a] | 12.1 | 11.3[b] | .. | .. | .. | .. |
| Percaprylic | 95 | 31–31.5 | 9.98 | 9.82 | 59.5 | 58.9 | 10.1 | 10.2 |
| Perpelargonic | 99 | 35–35.5 | 9.18 | 9.18 | 62.0 | 61.4 | 10.4 | 10.7 |
| Percapric | 95 | 40.8–41.4 | 8.50 | 8.52 | 63.8 | 64.0 | 10.7 | 10.8 |
| Perhendecanoic | 95 | 47.5–48 | 7.98 | 7.96 | 65.9 | 65.6 | 11.0 | 11.8 |
| Perlauric | 97 | 52 | 7.40 | 7.50 | 66.7 | 66.6 | 11.2 | 11.0 |
| Pertridecanoic | 92 | 53.7–54.3 | 6.95 | 6.90 | 67.8 | 68.0 | 11.4 | 11.5 |
| Permyristic | 85 | 56 | 6.54 | 6.56 | 68.8 | 68.6 | 11.5 | 11.4 |
| Perpalmitic | 61 | 61–61.5 | 5.87 | 5.86 | 70.5 | 69.7 | 11.8 | 11.6 |
| Perstearic | 66 | [c] | ... | ... | .. | .. | .. | .. |

[a] See reference 9. The melting point we obtained on a product containing 95% percaproic acid was 6–7°. [b] An analytically pure sample of percaproic acid could not be prepared. It apparently decomposes even at 0°. [c] Perstearic acid could not be separated from unreacted stearic acid.

substantially pure *cis*-9,10-epoxystearic acid (65% yield); oxirane oxygen 5.20% (calcd. 5.36%); iodine number 0 (calcd. 0); neutralization equivalent, 295 (calcd. 298); and m.p. 58.5–59° (literature[16] 59.5°).

**Polarographic Behavior of Peracids.**—A Sargent model XXI polarograph was used to obtain the current–voltage curves. The capillary had *m*- and *t*-values of 3.13 mg. per second and 1.45 seconds, respectively, yielding a capillary constant of 2.29 mg.$^{2/3}$ sec.$^{-1/2}$. These values were obtained using an open circuit with the capillary dipping into the electrolytic solution maintained at 25 ± 0.1°.

For most of the work the electrolytic solution consisted of 0.3 *M* lithium chloride in 1:1 (by volume) absolute methanol–benzene. The modified H-cell,[17] containing 40 ml. of the electrolytic solution, had a resistance of 1175 ohms. All half-wave potentials were corrected for *IR* drop and were measured against a saturated calomel electrode. For some of the polarographic measurements an electrolytic solution consisting of 0.25 *M* ammonium acetate in glacial acetic acid also was used.[18]

Details of the polarographic procedure have been described in a previous publication.[17] Polarograms of purified peracid samples were obtained in duplicate or triplicate in both electrolytic solutions. To minimize the interference of extremely high maxima exhibited by concentrated solutions of peracids, dilute solutions (4–20 × $10^{-3}$ *M*) were used. At these low concentrations the maxima were sufficiently suppressed so that reliable wave height measurements could be obtained provided the wave heights were measured in the flat portion of the curves (applied voltage range from −0.9 to −1.5 v.). All of the peracids examined exhibited half-wave potentials in the narrow range of 0.00 to −0.06 v. *vs.* the saturated calomel electrode and thus resembled the acyl peroxides[17] and peracetic acid in their polarographic behavior.[17]

TABLE II

PSEUDO-FIRST ORDER SPECIFIC REACTION RATE CONSTANTS FOR REACTION OF PERACIDS WITH METHANOL AT 25°

| Peracid | Concn. in moles/l. × $10^3$ | Specific reacn. rate constant, $k \times 10^3$ min.$^{-1}$ |
|---|---|---|
| Percaprylic ($C_8$) | 20.4 | 1.03 |
| Perpelargonic ($C_9$) | 10.4 | 1.34 |
| Percapric ($C_{10}$) | 5.5 | 1.76 |
| Perhendecanoic ($C_{11}$) | 12.7 | 0.93 |
| Perlauric ($C_{12}$) | 4.4 | 1.41 |
| Pertridecanoic ($C_{13}$) | 6.5 | 1.05 |
| Permyristic ($C_{14}$) | 10.9 | 1.05 |
| Perpalmitic ($C_{16}$) | 4.2 | 1.92 |

## Results and Discussion

All the peracids listed in Table I, with the exception of percaproic acid (which we were unable to purify completely), are new compounds. Since no information was available in the literature on the properties of long-chain peracids for comparison with those of our products, it was necessary to demonstrate unequivocally that an organic peracid, rather than some other peroxide type, was in fact being obtained.

Peroxide oxygen analysis on the analytically pure products showed that *exactly* one oxygen atom was introduced into the fatty acid molecule. That the oxygen was exclusively in the carboxyl group and not in the alkyl chain was shown by reduction of the peracid to the corresponding aliphatic carboxylic acid in almost quantitative yield. To eliminate the possibility that small quantities of oxygen were in the chain (derived possibly from a hydroperoxide group), the reduced peracid was analyzed for hydroxyl oxygen. None was detected. Finally, it was shown that the long-chain peracids are capable of converting a double bond to oxirane in high yield, a reaction characteristic of organic peracids. Since the reaction for preparing the long-chain peracids proceeds substantially to completion, the water-washed ether solution of crude peracid can be used directly for epoxidation and other reactions without isolating or purifying the peracid. The only contaminant is a small quantity of the corresponding carboxylic acid, which is also the product to which the peracid is converted.

Long-chain peracids are insoluble in water and soluble in ether and alcohols. They undergo fairly rapid decomposition in methanol (and probably other alcohols). The $C_6$–$C_{10}$ members are readily soluble in hydrocarbons at or above 0°. The longer-chain ones ($C_{11}$–$C_{16}$) are readily soluble in hydrocarbons at or above 25° and they are conveniently purified by crystallization at about 0°. The peracids have a lower solubility in sulfuric acid than do the corresponding carboxylic acids. Also, the peracids have a characteristically sharp, unpleasant odor which decreases in intensity with increasing chain length. They are irritating to the skin and mucous membranes and should be washed off immediately.

Organic peracids containing 6 or more carbon atoms appear to be considerably more stable than the well-known shorter-chain peracids, although this may be related to their higher purity. In the

(16) T. W. Findley, D. Swern and J. T. Scanlan, THIS JOURNAL, **67**, 412 (1945).

(17) C. O. Willits, C. Ricciuti, H. B. Knight and D. Swern, *Anal. Chem.*, **24**, 785 (1952).

(18) G. B. Bachman and M. J. Astle, THIS JOURNAL, **64**, 1303 (1942).

chain-length range from $C_8$–$C_{18}$, they can be stored for long periods at 0–5° without apparent change; percaproic acid is somewhat less stable and is preferably stored at −20°. At room temperature, the long-chain peracids decompose at a slow but significant rate. Thus, perlauric acid lost about 15% of its peroxide oxygen content when stored for one week at 25°. Some preliminary information on the decomposition of these substances in methanol–benzene solution is given in a later portion of this paper. A detailed kinetic investigation of their decomposition under various conditions, however, is now in progress and will be published later.

A plot of the melting points of aliphatic peracids against number of carbon atoms yields a smooth curve. (The melting points of the $C_2$–$C_6$ compounds were obtained from the literature.[8,9]) As is well known, the melting points of the corresponding carboxylic acids exhibit a saw-tooth curve. This suggests that peracids with both odd and even numbers of carbon atoms pack in the same way in the crystal. As would be anticipated, the melting points begin to level off at about $C_{16}$. The melting point for perbutyric acid ($C_4$) reported in the literature is considered to be low since the purity given for a compound with this melting point is 95.4%.[3] The minimum melting point (−13°) is exhibited by perpropionic acid ($C_3$).

In general, with the exception of formic acid, the acid-catalyzed reaction of carboxylic acids with 50% hydrogen peroxide is slow even with acids which are readily soluble, such as acetic, propionic and butyric. In concentrated sulfuric acid solution, however, peracid formation is extremely rapid. For example, with a 100% molar excess of hydrogen peroxide conversion of the carboxylic acid to peracid is quantitative as soon as the reactants are mixed; with a 50% molar excess, about one hour is required. Also, since peracid formation is an equilibrium reaction (eq. 1) the final concentration of water in the reaction mixture should not exceed about 25%, otherwise the

$$RCO_2H + H_2O_2 \rightleftharpoons RCO_3H + H_2O \qquad (1)$$

reverse reaction becomes significant and conversions drop. On the other hand, we have observed little difference in results in using 100% sulfuric acid instead of ordinary concentrated (95–96%), and 65% hydrogen peroxide instead of 50%, provided that the total water content does not exceed about 25% of the reaction mixture.

Aliphatic monocarboxylic acids, with the exception of formic acid which decomposes, behave as simple bases and give stable solutions in concentrated sulfuric acid (eq. 2).[19–21] The unexpectedly high rate of formation of peracids in concen-

$$RCO_2H + H_2SO_4 \rightleftharpoons RCO_2H_2^+ + HSO_4^- \qquad (2)$$

trated sulfuric acid medium is, therefore, probably a result of rapid nucleophilic attack by hydrogen peroxide on the highly electrophilic protonated fatty acid (eq. 3). Formic acid, on the other hand,

$$RCO_2H_2^+ + H_2O_2 \rightleftharpoons RCO_3H + H_3O^+ \qquad (3)$$

reacts rapidly with hydrogen peroxide (in the absence of sulfuric acid or other acidic catalyst) probably because protonated formic acid already is present in small amounts in equilibrium with formic acid (eq. 4).[22]

$$2\ HCO_2H \rightleftharpoons HCO_2H_2^+ + HCO_2^- \qquad (4)$$

The nucleophilic character of hydrogen peroxide under alkaline[23] and acidic[12,24,25] conditions in the preparation of hydroperoxides[12,23,24] and short-chain peracids[25] has been suggested. It is reasonable to assume that hydrogen peroxide behaves similarly in sulfuric acid. It would be of interest to determine the rate-controlling step in the reactions conducted in sulfuric acid solution but they proceed so rapidly that this objective appears difficult of attainment. By using $O^{18}$ in the acid, it has been shown[25] that hydrogen peroxide, in keeping with its nucleophilic character, contributes both its oxygen atoms to the carboxylic acid which undergoes acyl–oxygen fission. Thus, peracid formation is analogous to esterification and hydrolysis.[25]

Methyl esters of long-chain fatty acids also are converted to peracids by reaction with 50% hydrogen peroxide in concentrated sulfuric acid solution. The reaction proceeds slightly more slowly than with the free carboxylic acid and conversion to peracid is not as high. Thus, whereas lauric acid can be almost quantitatively converted to perlauric acid within one hour with a 50% molar excess of hydrogen peroxide, the conversion of methyl laurate is only 80–85%. The only advantage in using the methyl ester instead of the free acid is that the former has a somewhat greater solubility in the reaction mixture, which is important when the acid contains sixteen or more carbon atoms. In attempting to prepare perstearic acid, for example, the low solubility of stearic acid resulted in a highly viscous reaction mixture with poor heat transfer properties. In most cases, it was impossible to avoid the formation of hot spots with consequent carbonization of the entire mass. In the reaction of methyl stearate with hydrogen peroxide in sulfuric acid carbonization occurred less frequently, but was not completely eliminated.

Hydrogen peroxide is considerably more nucleophilic than water. For example, if methyl laurate (10.7 g., 0.05 mole) is dissolved in 20–25 g. of 76–95% sulfuric acid at room temperature and the solution is poured onto ice after one to three hours, the water-insoluble product consists of about 40% lauric acid and 60% methyl laurate. On the other hand, if the methyl laurate is dissolved in 20 g. of 95% sulfuric acid and 5.1 g. of 50% hydrogen peroxide is added (final sulfuric acid content about 85%) 80–85% of the methyl laurate is converted to perlauric acid after one hour.

**Polarographic Behavior.**—Figure 1 shows the polarographic waves obtained with perlauric acid in the methanol–benzene electrolytic solution. Similar waves were obtained with all eight per-

(19) A. Hantzsch, *Z. physik. Chem.*, **61**, 257 (1908).

(20) G. Oddo and A. Casalino, *Gazz. chim. ital.*, **47**, II, 200 (1917).

(21) R. J. Gillespie and J. A. Leisten, *Quart. Revs. (London)*, **8**, 40 (1954).

(22) H. B. Knight, R. E. Koos and D. Swern, THIS JOURNAL, **75**, 6212 (1953).

(23) H. R. Williams and H. S. Mosher, *ibid.*, **76**, 3495 (1954).

(24) A. G. Davies and A. M. White, *Nature*, **170**, 668 (1952); A. G. Davies, R. V. Foster and A. M. White, *J. Chem. Soc.*, 1541 (1953).

(25) C. A. Bunton, T. A. Lewis and D. R. Llewellyn, *Chemistry & Industry*, 191 (1954).

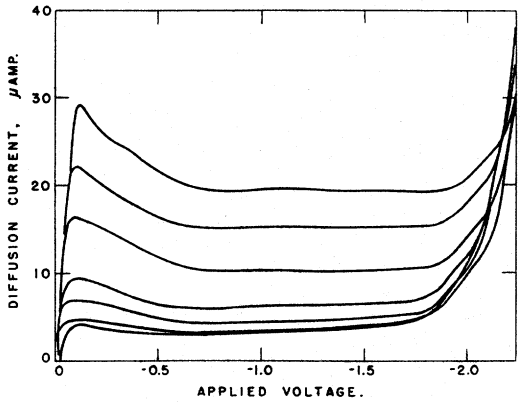


Fig. 1.—Polarograms of perlauric acid at half-hour intervals.

acids examined. During the recording of the polarogram of perlauric acid, it was observed that the polarographic wave height decreased if the peracid was left in contact with the methanol–benzene solution. The series of polarographic waves shown in Fig. 1 were obtained on the same sample of perlauric acid at half-hour intervals. The decrease in wave height indicated that the perlauric acid either was undergoing thermal decomposition or that it was reacting with mercury or one of the constituents of the electrolytic solution. To ascertain which of these was the cause of the decrease in perlauric acid concentration, the following experiments were performed. A series of methanol solutions containing identical concentrations of perlauric acid was prepared. These solutions were allowed to stand for different time intervals ranging from 0.5 to 2.5 hours; lithium chloride and benzene were then added and polarograms recorded. These polarograms showed that the perlauric acid wave height decreased at the same rate as had occurred when the peracid was allowed to stand in the electrolytic solution. This proved that the decrease in the concentration of the perlauric acid observed in the methanol–benzene electrolytic solution was not affected by the presence of mercury, lithium chloride or benzene. To establish whether the decrease in peracid concentration was due to thermal decomposition or reaction with methanol, weighed samples of perlauric acid were dissolved in benzene, left standing for several hours, methanol and electrolyte then were added and polarograms recorded. Since no diminution of wave height occurred with these samples it was concluded that the decrease in the perlauric acid concentration was caused by its reaction with methanol. Similar results were obtained with the other peracids reported in this study.

These observations suggested that the polarographic method might be used to follow the reaction of the peracids with methanol and possibly to determine the kinetics of these reactions. A weighed sample of a peracid was placed in the methanol–benzene electrolytic solution and after ten minutes of degassing with nitrogen, polarographic waves were obtained at 15-minute intervals. Since the methanol concentration was much greater than the peracid concentration it was assumed to be constant throughout the reaction. Therefore, the reaction was plotted as a pseudo-first order type. A plot of $\log a/(a - x)$ against time in minutes, where $a$ is the original (extrapolated) wave height at zero time and $x$ is the wave height at any given time interval, yielded straight lines. Figure 2 shows the plots for permyristic, perpelargonic, percapric and perpalmitic acids (curves I, II, III and IV, respectively). Although the points for the initial stages of the reaction deviated from the straight lines, the high linear correlation of the points after the first 30 minutes definitely would indicate a pseudo-first order reaction.

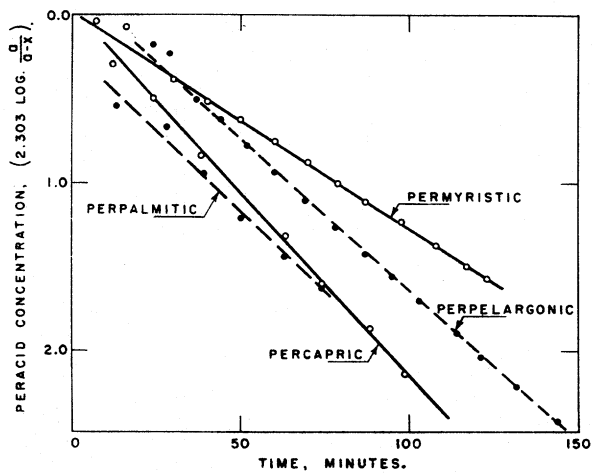


Fig. 2.—Pseudo-first order plot of decomposition of peracids with time in methanol–benzene solution.

The calculated specific reaction rate constants for the reaction of the eight peracids with methanol are shown in Table II. This table shows that the specific reaction rate constants for the reaction of these peracids with methanol are all of the same magnitude and vary from 0.93 to $1.92 \times 10^{-3}$ $\text{min}^{-1}$. In addition, the data indicate that although the length of carbon skeleton varied from 8 to 16 carbon atoms and the peracid concentration was varied fourfold this had little effect on the reaction rate constants. The natures of the reaction products are not known at present. They are not polarographically reducible, however, in the voltage range of the electrolytic solution for no new waves appeared during the reactions.

Since the peracids react with the methanol of the electrolytic solution, a search was made for an inert electrolytic system. Acetone solutions containing lithium chloride, although unreactive toward the peracids, were not satisfactory because they yielded ill-defined waves. Glacial acetic acid containing 0.25 $M$ ammonium acetate, however, yielded well-defined peracid waves which were stable with time. This electrolytic solution had been used previously by Bachman and Astle for the determination of metal ions.[18] As with the methanol–benzene solution the wave heights obtained in this system were directly proportional to concentration. The half-wave potentials of the peracids in the glacial acetic acid solution were in the same narrow range (0.00 to −0.06 v.) as those previously obtained with the methanol–benzene system.