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# A New Synthesis of Peracetic Acid

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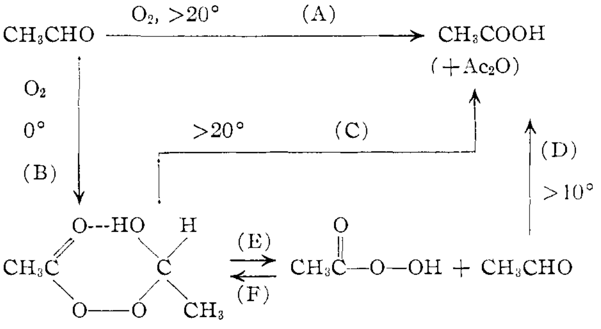
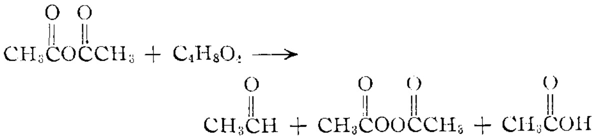
An efficient two-step synthesis of a water-free solution of peracetic acid in an inert solvent is described. In this synthesis, acetaldehyde is autoxidized at low temperature to an intermediate peroxide, acetaldehyde monoperacetate, which is then pyrolyzed to peracetic acid and acetaldehyde which are separated rapidly in a fractionating column.

Peracetic acid is potentially a very cheap epoxidizing reagent with great commercial potential, but its use in oxidations, especially epoxidations, has been limited by the presence of undesirable materials such as water, hydrogen peroxide and strong acids, all of which are difficult to remove.[1,2] We have found that water-free solutions of peracetic acid in inert solvents can be prepared in high efficiency from acetaldehyde and molecular oxygen. Furthermore, these solutions can be used to prepare epoxides in yields comparable to those obtained from perbenzoic acid or monoperphthalic acid. The present paper will describe the synthesis of peracetic acid and other papers will describe its use as a reagent.

**Oxidation of Acetaldehyde.**—Although Jorissen and van der Beek[3] succeeded in making perbenzoic acid by autoxidation of benzaldehyde, there is little in the literature for an analogous synthesis of peracetic acid.[4] Oxidation at temperatures above 20° (reaction A) gives acetic acid and sometimes also acetic anhydride. Oxidation at temperatures about 0° (reaction B) gives an unstable peroxide. Galitzenstein and Mugdan[5] showed that this peroxide could be prepared in high efficiency if care were taken to keep the temperature low and to avoid certain catalysts, particularly manganese ions or water, which caused decomposition of the peroxide into acetic acid and acetic anhydride (reaction C). They found that the peroxide precipitated from the acetaldehyde solution at higher conversions. These colorless crystals could be filtered off, but they were stable only when kept cold. If allowed to warm up to room temperature, they melted with vigorous decomposition. Solutions of the peroxide also had to be kept cold to avoid the rapid, exothermic reaction C. Galitzenstein and Mugdan believed that the crystals were those of peracetic acid, since Baeyer and Villiger[6] had postulated that peracids were intermediates in the autoxidation of aldehydes. Their product was not peracetic acid, however, because the properties of their compound were markedly different from those previously reported for peracetic acid by D'Ans and Frey.[7] The latter workers prepared peracetic acid from acetic acid and hydrogen peroxide and obtained it in a high state of purity by repeated distilling, freezing and centrifuging. In contrast to the unstable peroxide of Galitzenstein and Mugdan, they found peracetic acid to be reasonably stable at room temperature whether in the form of the pure liquid or in aqueous solution. Only when heated to its boiling point (110°) did it undergo violent decomposition to acetic acid and oxygen.



The nature of the crystalline peroxide formed in the low-temperature oxidation of acetaldehyde was more carefully investigated by Lösch.[8] He found it to have a melting point of 20–22°, whereas peracetic acid melts at 0°. When he allowed a sample of the unknown peroxide to decompose slowly under controlled conditions, he found that no gas was evolved, and the product was acetic acid of 98% purity. The original peroxide must therefore have had the same empirical formula as acetic acid. Lösch found the peroxide to have a molecular weight of about 105 and to contain 14 to 15% active oxygen. These values are admittedly only approximate, since the handling of such an unstable peroxide in a quantitative manner is extremely difficult, but the results are sufficiently accurate to show that the peroxide has the empirical formula $C_4H_8O_4$, corresponding to the combination of one molecule of oxygen with two molecules of acetaldehyde. Additional evidence for this composition had been provided by Krug and Sixt,[9] who showed that in the low temperature autoxidation of acetaldehyde to a peroxide the reaction stops when one mole of oxygen has been absorbed for each two moles of acetaldehyde originally present. When Lösch treated the unknown peroxide with



$$CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 + C_4H_8O_4 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H + CH_3\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}CH_3 + CH_3\overset{O}{\overset{\|}{C}}OH$$

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

(2) S. Winstein and R. B. Henderson, "Ethylene and Trimethylene Oxides" in "Heterocyclic Compounds," edited by R. C. Elderfield, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 1–60.

(3) W. P. Jorissen and P. A. A. van der Beek, *Rec. trav. chim.*, **45**, 245 (1916).

(4) D. P. Young, *Chemistry & Industry*, **46**, 777 (1949); J. E. Bludworth, U. S. Patent 2,314,385 (1943).

(5) E. Galitzenstein and M. Mugdan, U. S. Patent 1,179,421 (1916).

(6) A. Baeyer and V. Villiger, *Ber.*, **33**, 1569 (1900).

(7) J. D'Ans and W. Frey, *ibid.*, **45**, 1845 (1912).

(8) H. Lösch, P. B. 52007, pp. 23, 101. Office of Technical Service, U.S. Dept. of Commerce, Washington, D. C.

(9) A. Krug and J. Sixt, German Patent 730,116 (1940)

acetic anhydride, he obtained acetaldehyde, acetic acid and diacetyl peroxide as the products. Since diacetyl peroxide and acetic acid are the products obtained by acetylating peracetic acid with acetic anhydride, Lösch concluded that the unknown peroxide was an addition compound of peracetic acid and acetaldehyde. This is a reasonable view, since peracetic acid is a very weak acid (approximating hydrogen cyanide in strength) and would, like alcohols, be expected to add readily to the carbonyl group of acetaldehyde to form a compound analogous to the hemi-acetals (reaction F). We have shown (see Experimental) that the peroxide obtained from the autoxidation of acetaldehyde is identical with that obtained from peracetic acid and acetaldehyde.[10] This structure is similar to that proposed as an intermediate in the reaction of a ketone and a peracid.[11] In our paper the peroxide is referred to as "acetaldehyde monoperacetate" or "AMP," and the structure is normally written to indicate the internal hydrogen bonding which undoubtedly occurs.

As a first step in developing a synthesis for peracetic acid, the authors studied the oxidation of acetaldehyde to AMP. In the course of this work, it was found possible to use AMP itself as an epoxidizing agent.[12] It is recognized that great care must be exercised in handling AMP. Bloomfield and Farmer[13] reported that a violent explosion resulted from stirring a slurry of AMP crystals. As a first precaution, care should always be taken to avoid the formation of AMP crystals. The peroxide should always be handled in solution. We have conducted tests on AMP solutions having concentrations as high as 62% by subjecting them to the action of blasting caps. None of the AMP solutions were detonated by the blasting caps. We have concluded that the AMP solutions can be safely handled as long as the temperature is kept low and no crystals are present.

For practical operation, the low-temperature oxidation of acetaldehyde is best carried out using a catalyst. The salts of certain heavy metals,[5,14,15] ultraviolet light[5,16] and ozone[17,18] have been used. All of these were investigated in the present study. Cobalt salts were by far the most active catalyst studied. Even with only 0.01% of cobaltous acetate present, the rate of oxidation to AMP at −10° was limited only by the mechanics of dispersing the oxygen. In spite of the well-known behavior of cobalt salts as catalysts for the decomposition of peroxides, the formation of by-product acetic acid was not excessive. Apparently, the low temperature made this side reaction negligible. At higher temperatures, however, the cobalt salts increased the rate of decomposition of AMP, and other catalysts therefore appear more desirable so that the stability of the AMP solutions can be maximized.

Ultraviolet light, which does not lower the stability of the peroxide, is also an excellent catalyst. Figure 1 shows a reaction rate curve for a batchwise oxidation conducted in a cylindrical Pyrex reactor that was irradiated with three 275-watt RS Sunlamps. When the reaction was stopped at 50% conversion, the efficiency (yield of AMP based on acetaldehyde consumed) was 95%. It was later found possible to conduct the oxidation in a continuous fashion. Continuous operation at 50% conversion also could be conducted at 95% efficiency.

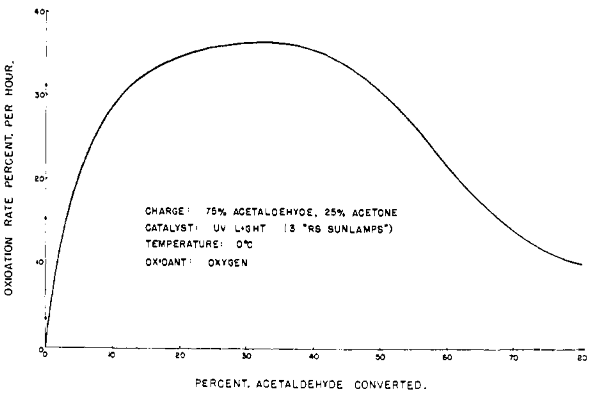

Fig. 1.—Oxidation of acetaldehyde to acetaldehyde monoperacetate.

Highly satisfactory results also were obtained using ozone as a catalyst for the oxidation. The oxygen or air stream was passed through an ozonator before being diffused into the acetaldehyde solution. With 2% ozone (by weight) in an oxygen stream it was possible to achieve the same reaction rate as with the previously described catalysis by ultraviolet light. Here, also, efficiencies of the order of 95% readily were obtainable.

**Preparation of Peracetic Acid Solutions.**—Having developed a satisfactory synthesis of AMP, the authors then studied its use for making peracetic acid. Attempts to oxidize AMP further to obtain free peracetic acid were unsuccessful. The oxidations came virtually completely to a standstill when half a mole of oxygen had been absorbed for each mole of acetaldehyde present.

There are a number of other possible reactions which the components of the system can undergo and which must be considered. As already pointed out, AMP will decompose spontaneously to two molecules of acetic acid (reaction C). This reaction is slow at 0°, but the rate increases rapidly with an increase in temperature. It is a highly exothermic reaction and requires no catalyst. The reac-

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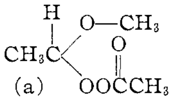
(10) Another peroxide has been prepared from peracetic acid and acetaldehyde. See J. D'Ans, K. Dossow and J. Mattner, *Angew. Chem.*, **66**, 633 (1954). These workers prepared a peroxide, m.p. −21 to −19°, in toluene solution *in the presence of methanol* at low temperature. It is interesting to note that all their analyses correspond very closely to that expected from a compound of the structure (a) whereas the analyses are not in very good agreement with their proposed structures.


(a)

(11) W. von E. Doering and E. Dorfman, THIS JOURNAL, **75**, 5595 (1953).

(12) See B. Phillips and P. S. Starcher, U. S. Patent 2,785,185 (1957).

(13) G. F. Bloomfield and E. H. Farmer, *J. Soc. Chem. Ind.*, **54**, 125T (1935).

(14) Consortium für Electrochemische Industrie, French Patent 460,972 (1913); German Patent 272,738 (1913).

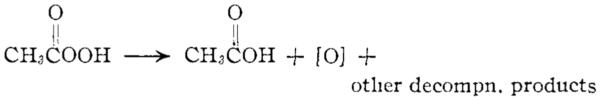
(15) H. Wieland, *Ber.*, **54B**, 2353 (1921).

(16) Consortium für Electrochemische Industrie, British Patent 16,849 (1913); German Patent 269,937 (1912).

(17) E. Briner and A. Lardon, *Helv. Chim. Acta*, **19**, 850, 1062 (1936).

(18) F. G. Fischer, H. Düll and J. L. Volz, *Ann.*, **486**, 80 (1931).

tion of peracetic acid and acetaldehyde can give rise both to acetic acid (reaction D) and also to reformation of AMP (reaction F). Both of these reactions were shown to occur and must be suppressed in a practical process for the preparation of peracetic acid. Finally peracetic acid itself will decompose to a number of products, chief of which is acetic acid.[19] The last reaction is catalyzed by many metal ions, even in minute concentrations.



$$CH_3\overset{O}{\overset{\|}{C}}OOH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OH + [O] + \text{other decompn. products}$$

It can be seen from the above discussion that the conversion of AMP into peracetic acid was a problem which was dual in nature. The AMP first had to be broken down into peracetic acid and acetaldehyde while avoiding the formation of acetic acid. The peracetic acid and acetaldehyde then had to be separated before they could interact to produce acetic acid or to reform AMP. Furthermore, this process had to be accomplished under conditions which avoided the undue formation of acetic acid by direct decomposition of peracetic acid.

Since solutions of AMP are relatively stable (with respect to retaining peroxide content) at 0°, attempts were made to ascertain whether or not reactions E and F were such as to favor the removal of acetaldehyde by distillation under reduced pressure. In the absence of a catalyst the removal of acetaldehyde while maintaining the solution at 0° was extremely slow. However, the addition of a strong acid catalyst allowed the removal of acetaldehyde and liberation of peracetic acid. Although this method allows the preparation of acetaldehyde-free peracetic acid, it is not an ideal answer to the problem. The long reaction time (4–7 hours) lowers the yield and makes the development of a continuous process difficult.

Surprisingly, we found that it was possible to decompose the AMP thermally without a catalyst and also to achieve separation of the resulting peracetic acid and acetaldehyde before they could react to form acetic acid. For example, a solution of AMP in acetone was fed continuously into a still kettle containing ethylbenzene under reflux at 70° and 70 mm. pressure. A 69% yield of peracetic acid was obtained as a dilute ethylbenzene solution by partially condensing the distillate and allowing the more volatile acetaldehyde and acetone to be condensed in the cold traps. This method is useful for obtaining peracetic acid in solvents which boil higher than peracetic acid.

Vapor-phase pyrolysis was found to be an excellent method for converting AMP to peracetic acid. The AMP solution was fed continuously to a heated zone under conditions which resulted in complete and instantaneous vaporizing of the solution. Thermal breakdown of the AMP occurred simultaneously. The vapors which now contained peracetic acid, acetaldehyde and solvent were then passed through a condenser or dephlegmator, where partial condensation occurred. Peracetic acid and solvent were the predominant components of the condensate, while the acetaldehyde went past the dephlegmator and was collected in the cold trap. The process was operated with solvents such as acetone and ethyl acetate, which boil below peracetic acid, as well as with solvents such as acetic acid, butyl acetate and dibutyl ether, which boil above peracetic acid. In the study of this method, it was found that complete pyrolysis was difficult to achieve at temperatures below 50°, and that, at temperatures above 250°, the formation of by-product acetic acid was excessive. Best results were obtained by passing the AMP solution through a tube which was externally heated to 100° with steam.

Improvement in the separation of peracetic acid from acetaldehyde was accomplished by using a fractionating column in place of the dephlegmator. With such a system, operated in continuous fashion, excellent yields of peracetic acid were obtained. In some experiments the yields of peracetic acid from AMP approached 100%. The fractionating column worked best when the solvent employed had a boiling point lying between that of acetaldehyde (21°) and peracetic acid (110°).

A pilot plant for the production of peracetic acid solutions was built and operated. All parts of the pilot plant were of stainless steel. The yields and efficiencies observed in this equipment were comparable to those obtained in laboratory-scale equipment.

## Experimental

**Preparation of AMP in a Glass Oxidizer.**—A solution of acetaldehyde (262 g.) and solvent (87 g. of ethyl acetate, acetone, acetic acid or other solvent) was charged to a vertical cylindrical Pyrex glass oxidizer (30 mm. i.d. × 125 cm.) equipped with a Pyrex glass jacket for cooling liquid (such as methanol–water at −10 to −15°) and fitted with a Dry Ice–acetone condenser at the top. The solution (at about 0°) was irradiated along the length of the oxidizer just outside the jacket with three Westinghouse type RS Sunlamps, and oxygen gas was introduced through a diffuser into the bottom of the oxidizer. Reaction occurred with rapid absorption of oxygen. Figure 1 shows a typical rate curve. After approximately 2 to 2.5 hours, the concentration of AMP was approximately 50%. The oxidizer was then drained or, if a continuous operation was desired, fresh acetaldehyde–solvent solution was fed into the top of the oxidizer while product was removed from the bottom through a discharge line which was elevated so as to maintain a constant level of solution in the oxidizer. In a typical continuous operation for 8 hours duration, acetaldehyde–solvent solution was fed at the rate of 167 ml./hr. into the oxidizer, and a peroxide solution containing 45% AMP and about 1% acetic acid (corresponding to 50% conversion) was removed.

Substitution of ultraviolet light with either 2% ozone (by weight) in the oxygen stream, or addition of 0.01% by weight of cobalt acetate to the acetaldehyde solution gave essentially the same results.

Air can be substituted for oxygen gas. By proper adjustment of the air input, the oxygen content of the blowoff gas can be kept below 3%. In two hours using ultraviolet light catalyst, the conversion of acetaldehyde to AMP was 30%, and the chemical efficiency was practically 100% as indicated by analyses for AMP and acetic acid.

**Preparation of AMP in a Stainless Steel Oxidizer.**—A mixture of acetaldehyde (704 g.) and ethyl acetate (704 g.) was charged to a cylindrical oxidizer and cooled to −2°. The oxidizer was a stainless steel pipe (3 in. × 4 ft.) jacketed with a larger pipe (4 in.) through which cooling liquid was circulated. Through the center of the oxidizer was a Pyrex pipe ($2^3/_8$ in.) which contained a 40-watt Westinghouse Fluorescent Sunlamp (4 ft. long) for irradiation of the reaction mixture. Oxygen was introduced through a diffuser

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(19) F. P. Greenspan and D. H. MacKellar, U. S. Patents 2,590,856 (1952) and 2,609,391 (1952).

into the bottom of the oxidizer. The oxygen absorption decreased from 50 to 22 l./hr. in 3.5 hours, when the reaction was terminated. Analysis of the product indicated an AMP content of 38% and no acetic acid. The conversion was 66%, and the chemical efficiency was practically 100%.

**Preparation of Acetaldehyde-free AMP in Butyl Acetate.**—Acetaldehyde (300 g.) and glacial acetic acid (100 g.) were charged to the glass oxidizer and oxidized with oxygen gas at 0 to +4° using ultraviolet light catalyst for two hours and 50 minutes to give a solution containing 53% AMP. The solution was added at 0° to 120 g. of butyl acetate. The acetaldehyde was removed under reduced pressure (10 mm.), the kettle being kept at 0° throughout the operation. The resulting solution had the following composition: 48% AMP, 25% acetic acid and 27% butyl acetate.

**Removal of Excess Acetaldehyde from a Solution Containing AMP.**—A solution (558 g.) of AMP was prepared by the low temperature oxidation of acetaldehyde in ethyl acetate. The solution by analysis contained 65 g. of acetaldehyde, 16.7 g. of acetic acid and 156 g. of AMP. The solution was fed to the bottom of a 0.27-in. i.d. stainless steel pipe (50 in. long) at the rate of 1320–1500 ml./hr. at a pressure of 80–85 mm. The pipe was heated by refluxing fluorotrichloromethane in an outer jacket, so that the mixture of liquid and vapor issuing from the pipe was at a temperature of 22–23°. From the pipe the product passed through a "cyclone" separator, and the residue was collected in a receiver maintained at −5°. The distillate was collected in a receiver immersed in a Dry Ice–acetone-bath. At the end of the addition of the AMP solution, 50 g. of ethyl acetate was run through the system as a purge.

There was collected as residue product 407 g. of solution analyzing 38.1% AMP. The product contained 9.5 g. of acetaldehyde which was not separated. The recovery of AMP was quantitative.

**Preparation of Peracetic Acid in Acetone.**—Three hundred seventy-five grams of an acetone solution containing 48.6% AMP, 7.7% acetic acid and 0.1% of Victor Stabilizer No. 53 was fed at the rate of 160–200 ml./hr. through a steam-heated stainless steel coil vaporizer into the middle of a laboratory distillation column containing stainless steel protruded packing. The column was operated at a pressure of 150 mm. with a head temperature of 14–15°. Acetone was fed at the rate of 160–240 ml./hr. through a steam-heated vaporizer into the column about one inch from the bottom. During the run, there was collected continuously 357 g. of distillate containing no acetic or peracetic acids, and from the bottom of the column 392 g. of acetone solution containing by analysis 27.9% peracetic acid and 9.1% acetic acid. The yield of peracetic acid based on the AMP fed to the column was 95%.

**Preparation of Peracetic Acid in Ethyl Acetate.**—A solution (356 g.) analyzing 46.9% AMP and 5.2% acetic acid in ethyl acetate and containing 0.1% added Victor Stabilizer No. 53 was fed through a steam-heated vaporizer into the middle of a 3-ft. stainless steel packed column at the rate of 200 ml./hr. The column was operated at a pressure of 70 mm. with a head temperature of 16–19°. Ethyl acetate was fed through a steam-heated vaporizer into the column about one inch from the bottom at the rate of 180–240 ml./hr. During the run, there was collected from the bottom of the still 413 g. of ethyl acetate solution analyzing 24.5% peracetic acid and 5.8% acetic acid. The yield of peracetic acid based on the AMP fed to the column was 97%.

**Preparation of Peracetic Acid from AMP by Complete Vaporization and Partial Condensation in a Dephlegmator.**—A solution (461 g.) of AMP in acetone, prepared by oxidation with ultraviolet light catalyst similar to the experiments described above, freed of unreacted acetaldehyde, was found by analysis to be 57.8% AMP. This solution was fed dropwise over one hour and thirty-five minutes to a one-liter four-necked glass flask which was maintained at 95–98° by external steam heating and under a pressure of 150–152 mm. Simultaneously, there was fed during this period a total of 200 ml. of acetone to the flask. Immediate volatilization of both feeds occurred on striking the hot flask, and the vapors were led through a steam-heated glass tube to a dephlegmator which was an up-draft glass Friedrich condenser cooled with tap water at approximately 15°. There was collected 345 g. of condensate which analyzed 35.5% peracetic acid (123 g., 73% yield). The vapors from the dephlegmator were passed through a trap cooled by ice-water, where 36 g. of condensate analyzing 16.9% as peracetic acid was collected, and then the vapors were passed through a trap cooled by a Dry Ice–acetone mixture, where 231 g. analyzing 1.7% as peracetic acid was further collected. The recovery of peroxide was 79%.

The condensate from the dephlegmator was then added back through the apparatus under the same conditions over one hour and two minutes while 190 ml. of acetone was fed simultaneously, and there was collected as condensate from the dephlegmator 367 g. which analyzed 32.3% peracetic acid. The over-all yield of peracetic acid from AMP was 71%.

**Preparation of Peracetic Acid at Low Temperature with a Sulfuric Acid Catalyst.**—Oxygen was introduced through a diffuser into a flask containing an agitated mixture of acetaldehyde (4 moles) and acetic acid (1 mole) at a temperature of approximately −10°. The flask was irradiated with a 275-watt Westinghouse sunlamp throughout the oxidation. After 5.75 hours the reaction mixture was diluted with 400 g. of cold chloroform and 20 g. of acetic acid containing 1.25 g. of sulfuric acid. Acetaldehyde was then removed from the mixture at a kettle temperature of 0° to 5° by distilling under reduced pressure (10–20 mm.) on a 3-ft. column equipped with a dephlegmator cooled to −40°. Acetaldehyde and chloroform were removed until 267 g. of peracetic acid solution remained in the kettle. Analysis of the cold solution indicated a peracetic acid content of 24%. After standing at room temperature for a few hours, the peroxide content dropped to the equivalent of 19.3% peracetic acid, indicating a small amount of AMP had not been decomposed previously.

**Preparation of an Ethylbenzene Solution of Peracetic Acid in a Conventional Still.**—A solution of 300 g. of acetaldehyde and 100 g. of acetone was oxidized with oxygen at low temperature, yielding a solution containing 50.4% of AMP. The excess acetaldehyde was removed from the solution under reduced pressure (10 mm.) at a temperature of −5 to 0°. The resulting solution (365 ml.) was added dropwise over a period of 2.75 hours to a still kettle containing originally 1710 g. of ethylbenzene. The still kettle was equipped with a 4-ft. packed column, and the contents of the kettle were kept boiling by maintaining a kettle temperature of 70° under 72–74 mm. pressure. At the stillhead, there was continuously removed by partial condensation with a water-cooled condenser 1001 g. of solution containing 75 g. of peracetic acid. The yield, based on AMP, was 69% of the theoretical.

**Preparation of AMP from Peracetic Acid and Acetaldehyde.**—A solution of 265 g. of ethyl acetate and 206 g. of a 28.3% solution of peracetic acid (58.5 g., 0.77 mole of peracetic acid) in acetic acid was cooled to 0°, and then 45 g. (1.02 moles) of cold acetaldehyde was added slowly with cooling to maintain the temperature below 1°. This solution was allowed to stand at 0° for five minutes and then was distilled at −5 to 0° for one hour at 6–10 mm. There was obtained 90 g. of distillate, caught in a receiver cooled to −70°, which contained 18.0 g. of acetaldehyde and analyzed for peroxide equivalent to 2.5 g. of peracetic acid. The residue solution (425 g.) from the distillation acted exactly like dilute solutions of AMP prepared by oxidation of acetaldehyde solutions. A small sample allowed to warm slowly to about 20° began a rapid exothermic decomposition. The residue solution analyzed for peroxide equivalent to 50.6 g. of peracetic acid or 80.0 g. of AMP. A sample (1.27 g.) was added to 50 g. of water, heated at 50° in a closed flask for 30 minutes, and then analyzed for peroxide. The peroxide content corresponded to 0.96% (4.1 g.) of peracetic acid in the residue. The results of the analysis of the residue indicate that 28 g. of acetaldehyde was bound by the peracetic acid as AMP. This checks very closely with the amount of acetaldehyde (27 g.) which was not recovered in the distillate.

To 10 g. of a 27.2% solution of peracetic acid in ethyl acetate (0.0358 mole of peracetic acid) at −5° was added 2 g. (0.0454 mole) of acetaldehyde. The resulting solution was held at −5 to 0° for five minutes and then cooled to −78°. A white crystalline solid formed slowly over a period of about 15 minutes. The solution was decanted off and the solid washed four times with cold (−78°) ethyl ether. After the final wash, the ether was sucked off through a sintered glass diffuser and the remaining solid dried at −10° for 15 minutes with a vacuum pump. There was obtained 1.4 g. of fluffy white crystals, m.p. 21.5–22.5°.

Solid AMP, m.p. 22–23°, was obtained by cooling the product of the oxidation of acetaldehyde in ethyl acetate solution (as described above) to −78°, and then washing the crystals with cold ether. The solid AMP from the two preparations was mixed as ether slurries and dried under vacuum at −10°. The m.p. of this mixture was 22–23°.

**Preparation of Peracetic Acid from AMP at Various Temperatures.**—Several experiments were performed on AMP solutions of 30 to 40% concentration in ethyl acetate freed of excess acetaldehyde as described above. These solutions were fed at the rate of 100 to 125 ml./hr. through a jacketed glass coil which was heated by a liquid under reflux in the jacket. The temperature in each run was fixed by the choice of the liquid used for heating purposes. The coil was fabricated from 8-mm. o.d. glass tubing and had an internal volume of 48 ml. The pressure in the system was controlled at 200 mm. After going through the coil, the peroxide mixture, in most cases largely in the vapor phase, was led to an up-draft Friedrich condenser, which served as a dephlegmator. Free acetaldehyde, along with some solvent, went past the dephlegmator and was collected in a cold trap. The condensate from the dephlegmator, collected in an ice-cooled flask, consisted of peracetic acid, AMP, ethyl acetate and by-product acetic acid. By passing this condensate through the coil a second time the amount of unconverted AMP could be reduced and the peracetic acid content increased. The table summarizes the results of a series of these runs.

| Temp. of heating liquid, °C. | Pressure, mm. | Total peroxide recovered, % After 1st pass | After 2nd pass | Yield of peracetic acid, % After 1st pass | After 2nd pass |
|---|---|---|---|---|---|
| 50 | 200 | 82 | 74 | 21 | 44 |
| 150 | 200 | 69 | 66 | 34 | 55 |
| 172 | 200 | 64 | 61 | 46 | 54 |
| 255 | 200 | 14 | 9 | 3 | 6 |

**Determination of Peracetic Acid.**—A 1-2-g. sample of peracetic acid solution is introduced into an erlenmeyer flask containing a mixture of 60 ml. of acetic acid and 5 ml. of saturated aq. potassium iodide solution. The peroxide oxidizes iodide ion to free iodine. The flask is swirled briefly to mix the solutions and complete the reaction. The contents are immediately titrated with 0.1 *N* aq. sodium thiosulfate solution to a colorless end-point.

**Determination of AMP.**—A sample of a solution of AMP is analyzed exactly as that described for peracetic acid except that 60 ml. of 50% aq. sulfuric acid is substituted for 60 ml. of acetic acid.

**Determination of Solutions Containing AMP and Peracetic Acid.**—A sample of the solution is analyzed for total peroxide using the procedure outlined above for the determination of AMP. A second sample of 1–2 g. is added to a flask containing 50 ml. of water. The flask is stoppered, heated to 50° for 30 minutes, and cooled to room temperature. Then 50 ml. of acetic acid and 5 ml. of saturated aq. potassium iodide are added, and the flask is swirled and titrated with 0.1 *N* aq. sodium thiosulfate solution. The second analysis gives the amount of free peracetic acid, and the difference between the two analyses gives the AMP.

**Determination of Acetic Acid in Solutions of Peracetic Acid or AMP.**—The solution is first analyzed for peracetic acid or AMP as described above. Another sample (1–2 ml.) is introduced into an erlenmeyer flask containing 50 ml. of water. Pure acetaldehyde (15 ml.) is added to the flask and, after mixing, is allowed to stand for 10–15 minutes. All of the peroxide is converted to acetic acid. The flask contents are titrated with 0.5 *N* aq. sodium hydroxide solution using phenolphthalein indicator. The acetic acid present in the original solution is then equal to the total acetic acid, as determined by the second sample, minus the acetic acid which came from the decomposition of peroxide which was determined in the first sample.

**Determination of Unreacted Acetaldehyde in AMP Solutions.**—A sample (5 g.) of AMP solution is added to 50 ml. of distilled water in a flask. To this solution is added 10 ml. of an approximately 25% solution of peracetic acid. A blank is also prepared where exactly the same amount of peracetic acid solution is added to 50 ml. of water. Both solutions are stoppered and heated to 50° for 30 minutes. Then, after cooling, to each is added 50 ml. of acetic acid and 5 ml. of saturated aq. sodium iodide. Each solution is then titrated with 0.1 *N* sodium thiosulfate. The difference in titrations is used to calculate the unreacted acetaldehyde as

$$\%\ \text{acetaldehyde} = \frac{\text{Diff. in } \mathrm{Na_2S_2O_4}(\text{ml.}) \times N_{\mathrm{Na_2S_2O_4}} \times 4.4}{\text{wt. sample} \times 2}$$

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

# Conformational Analysis. II. Esterification Rates of Cyclohexanols[1]

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Rates of esterification of cyclohexanol, *cis*- and *trans*-4-*t*-butylcyclohexanol, *cis*- and *trans*-4-, *cis*- and *trans*-3- and *trans*-2-methylcyclohexanol, *cis*- and *trans*-4-phenylcyclohexanol, 3,3-dimethylcyclohexanol, 4,4-dimethylcyclohexanol and the acylic analogs butanol-2 and benzylmethylcarbinol with acetic anhydride and, in some cases, propionic anhydride and isobutyric anhydride in excess pyridine as the solvent have been determined. From those data, the conformational equilibrium constant for hydroxyl (concentration of cyclohexanol with equatorial hydroxyl over that with axial hydroxyl) is calculated to be about 2.4 corresponding to a free energy difference of 0.5 kcal./mole and the interaction energy of 1,3-diaxial methyl and hydroxyl is estimated at 2.15 kcal./mole. The consistency of the data is examined.

The importance of conformation on reactivity in cyclohexane systems was first pointed out in 1950 by D. H. R. Barton[2] in a paper which has been of incalculable benefit to subsequent workers during the last seven years. Among other things, Barton[2] pointed out that an equatorial substituent in cyclohexane is less hindered and therefore, in general, more reactive than an axial substituent.[3] His examples come largely from rigid systems, such as substituted decalins, steroids or terpenes in which the axial or equatorial nature of a substituent can be ascertained unequivocally. It was subsequently

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[1] Paper I in this series: E. L. Eliel and C. Pillar, THIS JOURNAL, **77**, 3600 (1955). The present paper is taken from the Ph.D. thesis of Carl A. Lukach and was presented in part before the Organic Division at the Meeting of the American Chemical Society at Atlantic City, N. J., September 19, 1956.

[2] D. H. R. Barton, *Experientia*, **6**, 316 (1950); see also D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953), and *Experientia Supplementum II*, 121 (1956); D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 44 (1956).

[3] For background information and explanation of terminology see: (a) W. Klyne, "Progress in Stereochemistry. I," Butterworths, London, England, 1954, Chapter 2. (b) W. G. Dauben and K. S. Pitzer in M. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 1. (c) H. D. Orloff, *Chem. Revs.*, **54**, 347 (1954).