dimethylcarbinol an explosive reaction occurred on addition of few drops of the concentrated peracid, in spite of careful cooling. After thorough purification—by twice allowing to stand overnight with an excess of concentrated permanganate solution, washing, drying with barium oxide and fractionating (collected between 101.6° and 102.5°)—this tertiary alcohol still showed the same explosive tendencies, indicating that impurities can hardly be considered responsible for this behavior. A more dramatic demonstration of potential dangers occurred when a repetition, with fourfold amounts, of the above methylisobutylcarbinol experiment resulted in a violent detonation. Local overheating leading to a cumulative reaction evidently represents a real danger, at least in this particular alcohol. The following experiments throw some additional light on the danger factors. 0.30 cc. of concentrated peracid (11.7 M H_2SO_5, 3.3 M H_2SO_4, 0.6 M H_2O_2, 5.3 M H_2O) was added to 4 cc. of each of the following, cooled in freezing mixture: (a) isoamyl alcohol, (b) 4 M H_2SO_4 (99.4%) in isoamyl alcohol, (c) methylisobutylcarbinol, (d) 4 M H_2SO_4 in methylisobutylcarbinol. Of the resulting solutions (c) exploded after about one minute and (d) a little later, both while remaining in the freezing mixture. (a) and (b) were taken to room temperature after fifteen minutes, and now (a) exploded after several minutes while (b) did not explode. Obviously the primary $C_5H_{11}OH$ is less reactive than the secondary $C_6H_{13}OH$ and the latter in turn is more stable than the tertiary $C_5H_{11}OH$. The apparent reduction of explosibility by the presence of considerable sulfuric acid (about 37.5%) may be caused by the dilution of the organic component. It should be noted that the permonosulfuric acid concentration used (about 0.8 M) as well as the sulfuric acid concentration are considerably higher than those encountered in the solutions described in the earlier part of this paper, and in which no explosive tendencies were ever observed, even though considerable quantities were handled.

The writer wishes to express his appreciation of the assistance rendered by Dr. Mary A. Bennett in some phases of the experimental work.

Summary

Methods for obtaining solutions of permonosulfuric acid in some of the lower alcohols, including isoamyl alcohol, and in acetonitrile have been described. Examples illustrating the nature of the slow decompositions taking place in such solutions have been given and it has been shown that at −12° solutions containing as much as 0.6 M H_2SO_5 are of convenient stability. Attention is called to the possibility of explosive reactions with secondary and tertiary alcohols, and generally in cases of too high concentrations of the peracid.

PHILADELPHIA, PENNA. RECEIVED NOVEMBER 12, 1936

[CONTRIBUTION FROM THE LANKENAU HOSPITAL RESEARCH INSTITUTE]

A New Method for the Preparation of Permonophosphoric Acid[1]

BY GERRIT TOENNIES

Permonophosphoric acid since its discovery in 1910 by Schmidlin and Massini[2] has received little attention although it is distinguished by a remarkable oxidizing power (lower manganese salts are oxidized, in the cold, to permanganate). The method of Schmidlin and Massini, consisting in gradually combining phosphoric anhydride and concentrated hydrogen peroxide in very small portions, is difficult on account of the violence of the interaction, and uncertain as to result in spite of its tediousness. The only other method proposed by Fichter and associates,[3] produces by anodic oxidation mixtures of alkali salts of H_3PO_5 and $H_4P_2O_8$ in solutions of potassium fluoride and therefore is of limited usefulness. The present experiments were undertaken with a view of simplifying the production of this interesting compound by moderating the reaction between phosphoric anhydride and hydrogen peroxide through the use of suitable inert diluents for the latter.

Of three solvents studied, ether, isoamyl alcohol and acetonitrile, only the last one gave satisfactory results. Acetonitrile is completely inert against phosphoric anhydride and it can be used to make solutions of hydrogen peroxide of high concentration and high stability.[4] In two parallel experiments, in which the components were used in ratios approximately corresponding to the assumed reaction

$$P_2O_5 + 2H_2O_2 + H_2O \longrightarrow 2H_3PO_5 \qquad \text{(I)}$$

phosphoric anhydride (5.55 and 5.18 mml., respectively,) was suspended in 1.5 cc. of acetonitrile (Merck reagent) and at low temperature (freezing mixture) an acetonitrile solution (1.10 and 1.05 cc.) containing hydrogen peroxide[5] (12.94 and 12.35 mml.) and water (4.03 and 3.84 mml.) was added slowly. Besides, 0.30 cc. of acetonitrile was

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[1] Aided by a grant for fundamental research from E. R. Squibb and Sons.

[2] Schmidlin and Massini, *Ber.*, **43**, 1162 (1910).

[3] Fichter and associates, *Helv. Chim. Acta*, **1**, 297 (1918); **2**, 3 (1919); S. Husain and J. R. Partington, *Trans. Faraday Soc.*, **24**, 235 (1928).

[4] G. Toennies and M. Elliott, results to be published shortly in THIS JOURNAL.

[5] Hydrogen peroxide of 80 to 90% concentration was prepared according to Hurd and Puterbaugh, THIS JOURNAL, **52**, 950 (1930).

added in the first case, and 0.30 cc. of acetonitrile containing 0.023 mml. of 2,4-dinitrobenzenesulfonic acid[6] in the other case. The purpose of this modification was to examine the possibility that the reaction between phosphoric anhydride and hydrogen peroxide might be catalyzed by strong acids, as it has been found that the reaction between aliphatic anhydrides and hydrogen peroxide in non-aqueous systems is highly susceptible to acid catalysis.[4] The phosphoric anhydride was in both instances energetically attacked and cooling was necessary for some time to keep the reaction mixture from exceeding room temperature. Some escape of gas was visible and the odor of ozone appeared, to which after a while the characteristic "peracid" odor (known from perbenzoic and permonosulfuric acid) was added. Analysis—by the methods previously (*cf.* preceding paper) used by the author for solutions of permonosulfuric acid—after twenty hours gave for the two solutions, respectively: peracid 56 and 57%, hydrogen peroxide 20 and 18.5%, total peroxygen 76.5 and 76.5%, all in terms of the hydrogen peroxide used. In terms of phosphoric anhydride the result is that 65.3 and 68.0%, respectively, have been converted into permonophosphoric acid. The agreement between the two experiments, surprisingly close for a heterogeneous reaction of this character, indicates the absence of acid catalysis as a rate determining factor, and the data further show that the desired reaction takes place to a satisfactory extent in acetonitrile and that no peroxide other than permonophosphoric acid, such as perphosphoric acid $H_4P_2O_8$,[2,3] is formed. It should be stated here that the conclusion that the peroxide (previously referred to as "peracid") formed is permonophosphoric acid, is based on the following considerations: (1) the evidence of Schmidlin and Massini[3] indicating that the compound resulting from interaction of phosphoric anhydride and hydrogen peroxide is permonophosphoric acid, (2) observations[4] that solutions of hydrogen peroxide in acetonitrile are extremely stable and show no evidence of formation of a peroxide which reacts rapidly with iodide in the manner observed here and which is indistinguishable from the analogous action of permonosulfuric acid, (3) acidimetric evidence (described in connection with the next experiment, ***vide infra***) that the acid left after removal of the peroxygen is H_3PO_4 and not HPO_3 which should result if the peracid present had the formula HPO_4, and (4) the qualitative observation that these acetonitrile solutions cause oxidation of Mn^{++} to MnO_4^- in the cold, a reaction which, according to the discoverers,[2] distinguishes permonophosphoric acid from other peroxides.

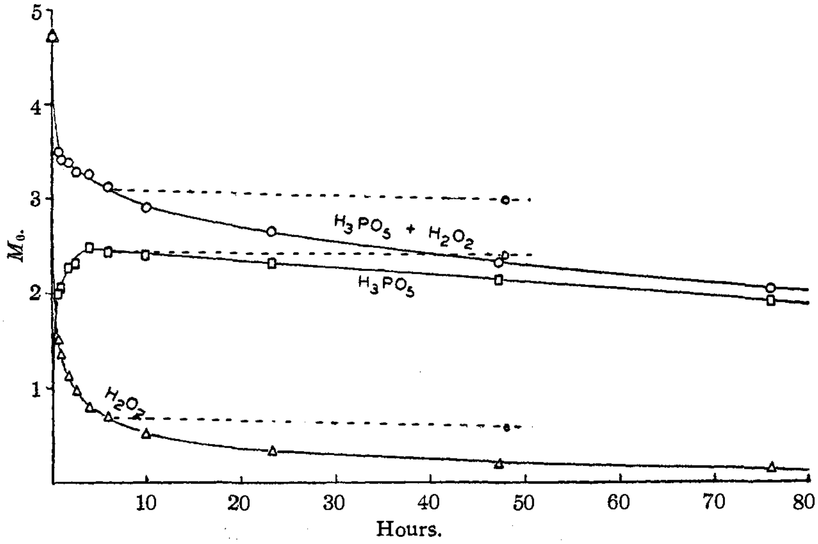

Fig. 1.—The reaction between phosphoric anhydride and hydrogen peroxide at room temperature (about 25°). M_0 indicates molarity in peroxygen, *e. g.*, 1 M H_3PO_5 or 1 M H_2O_2 = 1 M_0. The moment when the hydrogen peroxide was completely added has been taken as zero time. The dotted lines show the stabilizing effect of low temperature, obtained by keeping a part of the solution at about −12°.

The next experiment was designed to throw some light on the rate of formation of the peracid. To a suspension of 15.55 mml. of phosphoric anhydride in 4 cc. of acetonitrile, cooled in freezing mixture, 3.05 cc. of an acetonitrile solution containing 35.87 mml. of hydrogen peroxide and 11.34 mml. of water were added slowly during about five minutes. After three additional minutes the mixture was brought to room temperature and after forty-five minutes of standing, with occasional shaking, very little phosphoric anhydride remained undissolved. From this point on, 0.1-cc. samples were withdrawn periodically (by means of a Folin micro blood sugar pipet; the average deviation in the size of the sample obtained was ±0.15%) and analyzed. The data obtained are plotted in Fig. 1. They show that the bulk of the peracid is formed within the first hour, during the dissolving of phosphoric anhydride, that most of the loss of peroxide occurs during this period, and that even after the phosphoric anhydride has completely dissolved (about 100 minutes) additional peracid is formed. The yield of peracid at the maximum (four hours) is 60.5% in terms of phosphoric anhydride. Further work is planned to study the mechanism of the reaction and the factors influencing it. To determine if metaphosphoric acid, or its hypothetical per-derivative (HPO_4) might be present in the solution, acidimetric titrations were carried out as follows: about two hours after the beginning of the reaction 0.1-cc. samples were added to 0.8 cc. of 0.6 M dibenzyl sulfide in acetonitrile. This causes the transfer of the active peroxygen to dibenzyl sulfide, thus eliminating it as a disturbing factor in acidimetry since the resulting dibenzyl sulfoxide is relatively inert as an oxidizing agent. Titration with 0.05 N NaOH to the turning point of (a) methyl orange (*p*H 4) and (b) thymolphthalein (*p*H 10) gave the following results: (a) 4.07, 4.16 N, (b) 8.36, 8.58 N. The 1:1 ratio is in agreement with H_3PO_4 (and possibly

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(6) *Cf.* G. Toennies and M. Elliott, THIS JOURNAL, 57, 2136 (1935).

$H_4P_2O_7$) and suggests absence of appreciable amounts of a monobasic acid (HPO_3).

The relative stability at room temperature of this peracid in acetonitrile is remarkable in comparison with that of solutions of permonosulfuric acid in acetonitrile (*cf.* preceding paper). Since the peroxygen of H_3PO_5 is more active than that of H_2SO_5 it appears likely that the difference in stability is due to catalytic effects of the accompanying acids, inasmuch as H_3PO_4 is a weak acid compared with H_2SO_4. Just as permonosulfuric acid (*cf.* preceding paper), so also permonophosphoric acid can be kept in isoamyl alcoholic solution, the stability being of a similar order. Dilutions of the first two acetonitrile solutions described here with 10 volumes of isoamyl alcohol showed, in terms of the yields reported above, after three days at −11°, the presence of 51 and 50.5% (instead of initially 56 and 57%) of peracid and of 71.5% of peroxygen (instead of 76.5%) in both cases.

When instead of acetonitrile, ether or isoamyl alcohol was used as the medium for the interaction between hydrogen peroxide and phosphoric anhydride, the results were as follows. An ether solution, about 2.8 *M* in hydrogen peroxide and 0.85 *M* in water, left in contact, for twenty-four hours at room temperature, with an amount of phosphoric anhydride corresponding to the hypothetical reaction

$$P_2O_5 + H_2O_2 \longrightarrow HPO_3 + HPO_4 \qquad \text{(II)}$$

showed little action upon the solid phase. Analysis of the whole reaction mixture showed 2.5% of the hydrogen peroxide as such, 17% as peracid and a total peroxygen recovery of 26%. When the components were used in ratios corresponding to reaction (I) (2.5 *M* H_2O_2, 1.2 *M* H_2O) the phosphoric anhydride went into solution within two hours, forming an oily layer. Analysis showed a total recovery of 9.4% as peracid and 68% as hydrogen peroxide. After twenty hours the corresponding figures were 14 and 44% showing that formation of additional peracid proceeds much slower than loss of hydrogen peroxide. In similar experiments using isoamyl alcohol as the medium less than 2% of the hydrogen peroxide was converted into peracid.

Summary

A convenient method for the preparation of solutions of permonophosphoric acid, based on the heterogeneous interaction between phosphoric anhydride and hydrogen peroxide in acetonitrile, has been described and it has been shown that such solutions, even at room temperature, are relatively stable. When instead of acetonitrile, ether or isoamyl alcohol is used as the medium, the reaction between hydrogen peroxide and phosphoric anhydride is of negligible extent.

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[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

A Comparison of Hydrogen, Quinhydrone and Glass Electrodes in Magnesium Sulfate Solutions

BY E. S. AMIS AND J. L. GABBARD

The error of the glass electrode compared with that of the hydrogen electrode in solutions of various ions has received much attention,[1-8] and the rapid increase in its use in various *p*H studies and industrial processes justifies further investigation. Therefore, the authors have made a direct comparison of the hydrogen, quinhydrone and glass electrodes in buffered and unbuffered, except for small quantities of hydrochloric acid, magnesium sulfate solutions.

Apparatus and Materials

The glass electrodes having a resistance of the order of 10^7 ohms were blown of Corning 015 glass in the form of a thin bulb[1,9] on the end of a tube of ordinary soft glass and aged for at least twenty-four hours before using. The silver–silver chloride electrode of the reduced oxide type[10] was placed in the 0.1 *N* hydrochloric acid inside the glass electrode and served as the reference electrode. The hydrogen electrodes were made in the usual manner and the quinhydrone electrodes were made and cleaned as recommended by Morgan, Lammert and Campbell.[11] The hydrogen electrodes were also cleaned in this manner before being platinized. This cleaning process was repeated and the hydrogen electrodes were newly platinized before each series of measurements. The platinum black was removed from the hydrogen electrodes by the use of hot aqua regia. Two hydrogen and two quinhydrone electrodes were used in making the measurements. If the difference in potential between the two respective electrodes was not less than 0.2 mv., a new pair of electrodes was selected. The calomel electrode was prepared from the Leeds and Northrup chemicals especially purified for the purpose. Commercial tank hydrogen was purified as described by Dole.[4] Since

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