A new method for the preparation of peroxymonophosphoric acid

Tian Zhu, Hou-min Chang, and John F. Kadla

Abstract: A new method for the preparation of peroxymonophosphoric acid (H_3PO_5) has been developed. It utilizes a biphasic solution to moderate the vigorous reaction between phosphorous pentoxide (P_2O_5) and hydrogen peroxide (H_2O_2). P_2O_5 is suspended in carbon tetrachloride (CCl_4), and concentrated H_2O_2 is slowly added while being vigorously stirred at low temperature. Careful control of the reaction temperature through the slow addition of H_2O_2 is critical. Using typical preparation conditions (P_2O_5:H_2O_2 = 0.5:1, H_2O_2 70 wt %, 2°C, 120–180 min), ~70% of the H_2O_2 is effectively converted to H_3PO_5. Increasing the concentration of H_2O_2, as well as the mole ratio of P_2O_5:H_2O_2, leads to an even higher % conversion of H_2O_2 to H_3PO_5. The addition of glacial acetic acid to the P_2O_5:H_2O_2 suspension at the end of the 120–180 min reaction (P_2O_5:H_2O_2:CH_3COOH = 0.5:1:0.3) leads to the formation of peracetic acid in addition to H_3PO_5, and to an overall increase in the conversion ratio of total peroxy acids based on H_2O_2 (>95%).

Key words: peroxymonophosphoric acid, synthesis, stability, conversion ratio.

Résumé : On a mis au point une nouvelle méthode de préparation de l'acide peroxymonophosphorique (H_3PO_5). Elle fait appel à une solution biphasique pour modérer la réaction vigoureuse du pentoxyde de phosphore (P_2O_5) et du peroxyde d'hydrogène (H_2O_2). Le P_2O_5 est mis en suspension dans le tétrachlorure de carbone (CCl_4) et le H_2O_2 est ajouté lentement à basse température sous agitation vigoureuse. Il est critique de bien contrôlé la température de la réaction par une addition lente du H_2O_2. Utilisant des conditions de préparation typiques (P_2O_5:H_2O_2 = 0,5:1; H_2O_2 à 70% en poids; à 2°C; 120–180 min), environ 70% du H_2O_2 est effectivement converti en H_3PO_5. Une augmentation de la concentration du H_2O_2 ainsi qu'une augmentation du rapport molaire P_2O_5:H_2O_2 conduit à des pourcentages encore plus élevés de conversion du H_2O_2 en H_3PO_5. L'addition d'acide acétique glacial à la suspension de P_2O_5:H_2O_2 à la fin de la réaction de 120 à 180 min ((P_2O_5:H_2O_2:CH_3COOH = 0,5:1:0,3) conduit à la formation d'acide peracétique en plus du H_3PO_5 et à une augmentation globale du rapport de conversion globale en peroxyacides par rapport à la quantité de H_2O_2 utilisée (>95%).

Mots clés : acide peroxymonophosphorique, synthèse, stabilité, rapport de conversion.

[Traduit par la Rédaction]

Introduction

Peroxy acids are widely used, versatile oxidizing agents. The mechanisms of reactions involving peroxy acids have been extensively studied by a variety of techniques and have provided a fundamental understanding of autoxidation and other reactions involving peroxygen compounds (1,2). In spite of their importance as oxidants, the number of peroxy acids available for organic synthesis and oxidation chemistry is rather limited: peroxy formic acid and peroxy trifluoroacetic acid are formed readily in situ from hydrogen peroxide and the corresponding acid, whereas peracetic acid, *m*-chloro-peroxy benzoic acid (MCPBA), and the potassium salt of peroxymonosulfuric acid (OXONE®) are commercially available products.

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In addition to peroxymonosulfuric acid, several other inorganic peroxy acids have been utilized in oxidation reactions, e.g., pernitric acid (3) and peroxymonophosphoric acid (4–8). Peroxymonophosphoric acid was first prepared in 1910 by Schmidlin and Massini according to the following reaction (eq. [1]) (9):

$$[1] \qquad P_2O_5 + 2\ H_2O_2 + H_2O \longrightarrow 2\ H_3PO_5$$

However, the reaction was extremely vigorous, generating a large amount of heat, which rapidly decomposed the peroxy acid. As a result, only a small amount of peroxy acid could be obtained by this method. Subsequently, in 1937, Toennies tried to moderate the vigorous reaction by introducing acetonitrile as an "inert diluent", and claimed to obtain relatively stable solutions containing 51% peroxy acid at –11°C (10). However, problems concerning reproducibility exist, as hydrogen peroxide and peroxy acids are known to hydrolyze acetonitrile (eq. [2]) (11, 12).

$$[2] \qquad CH_3CN + H_2O_2 \longrightarrow [(CH_3C(NH)O_2H] \longrightarrow CH_3CONH_2 + [O]$$

As a result, the most widely used method for preparing H_3PO_5 is the hydrolysis of potassium or lithium

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peroxodiphosphate in a strong acid solution such as $HClO_4$ (eq. [3]) (13).

[3] $$P_2O_8^{4-} + H_2O \xrightarrow{HClO_4} H_3PO_5 + H_3PO_4$$

Unfortunately, the extreme reagents, combined with the high costs and the low peroxy acid yields have hindered its utilization in large-scale commercial applications. Several other methods for preparing H_3PO_5 have been utilized and include electrolysis of solutions of phosphates (14), as well as the reaction of $H_4P_2O_7$ with hydrogen peroxide (15). However, none of these methods gave reasonable yields of H_3PO_5. In this study we report a novel method for the preparation of H_3PO_5 in high yields.

Experimental

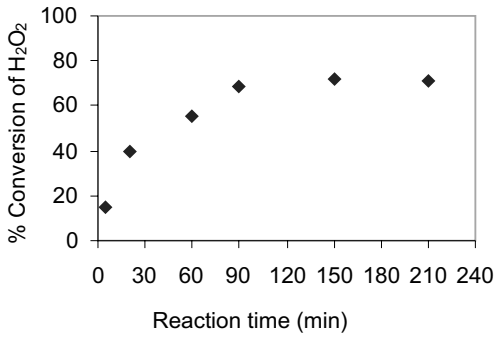
Materials

Phosphorous pentoxide (ACS reagent grade), carbon tetrachloride (ACS reagent grade), ceric sulfate (0.25 N), sodium thiosulfate (0.1 N), potassium iodide (1.0 N), Ferroin (1,10-phenanthroline ferrous sulfate), sulfuric acid (ACS reagent grade), and glacial acetic acid were purchased from Aldrich Chemicals and used as received. Hydrogen peroxide (70% and 90%) was obtained from FMC Corporation (Tonamanda, N.Y.). DTPA (diethylenetriaminepentaacetic acid) and DTMPA (diethylenetriaminepentamethylene phosphonic acid) were gifts from Buchman Chemicals Inc. All solutions were prepared in deionized water.

H_3PO_5 synthesis

In the preparation of H_3PO_5, P_2O_5 (17.0 g, 0.061 mole) was suspended in CCl_4 (10 mL), and the suspension was cooled in an ice bath to a temperature of ~2°C while being vigorously stirred. Aqueous hydrogen peroxide (0.121 mole, 5 mL of 70 wt %) was then added dropwise to the suspension, while the reaction temperature was carefully monitored. CAUTION: the addition rate of H_2O_2 must be carefully controlled to maintain the reaction temperature below 5°C. If the addition of H_2O_2 is too fast, the reaction is too vigorous and a violent exotherm can occur. However, if the addition of H_2O_2 is too slow, the P_2O_5 powder will tend to form larger aggregate particles, which are slow to react with the H_2O_2 and result in the accumulation of H_2O_2, and a potentially violent reaction can occur. Therefore, careful monitoring of the temperature while adding H_2O_2 at a sufficient rate to minimize P_2O_5 aggregation is required. Upon complete addition of H_2O_2 the biphasic reaction system was further stirred, for up to 3 h, to maximize peroxy acid yield (Fig. 1); prolonged mixing can lead to decreased H_3PO_5 yields. The aqueous phase was separated and the CCl_4 layer was extracted 2–3 times with deionized water (5 mL) to extract the H_3PO_5 along with phosphoric acid and hydrogen peroxide. The aqueous solutions were combined and the concentration of H_3PO_5 and H_2O_2 were determined by chemical methods. Accordingly, a sample of the reaction mixture (0.2 mL) was acidified with H_2SO_4 (200 mL, 1 N H_2SO_4) and cooled in an ice bath to permit titration within a temperature range of 0–10°C. Three drops of Ferroin solution was added, and the mixture was titrated with 0.1 N ceric sulfate until the disappearance of the salmon color. KI (5 mL, 1.0 N KI) was added, and the iodine liberated was titrated with sodium thiosulfate (0.1 N) to a starch end point. The amount (%) of peroxy acid and hydrogen peroxide was calculated according to eqs. [4] and [5], respectively.

Fig. 1. The effect of reaction time on % conversion of H_2O_2 to H_3PO_5 (P_2O_5:H_2O_2 = 0.5:1, 70 wt % H_2O_2, 2°C).



[4] $$\%\ \text{peroxy acid} = \frac{\text{mL } Na_2S_2O_3 \times 0.1\text{N} \times 0.038 \times 100}{\text{sample weight}}$$

[5] $$\%\ \text{hydrogen peroxide} = \frac{\text{mL } Ce(SO_4)_2 \times 0.1\text{N} \times 0.017 \times 100}{\text{sample weight}}$$

Results and discussion

Analogous to the work of Toennies (10), we have focused on moderating the reaction between H_2O_2 and P_2O_5 (eq. [1]). To avoid some of the problems associated with acetonitrile, we have chosen an inert solvent, CCl_4, which unlike acetonitrile is inert to most oxidants, and neither P_2O_5 nor H_2O_2 are soluble in it.

In a typical preparation, the reaction mixture was mixed for no longer than 3 h to maximize peroxy acid yield (Fig. 1). Careful control of the reaction system is required, as longer reaction times result in lower yields of H_3PO_5 because of the slow reaction between H_3PO_5 and H_2O_2 (eq. [6]).

[6] $$H_3PO_5 + H_2O_2 \longrightarrow H_3PO_4 + H_2O + O_2$$

By controlling the volume of CCl_4, the stirring speed, and the rate of the addition of hydrogen peroxide, approximately 70% of H_2O_2 was converted to H_3PO_5 at a mole ratio P_2O_5:H_2O_2 = 0.5:1. To the best of our knowledge such a high conversion ratio has never been reported.

Effect of P_2O_5:H_2O_2 on the preparation of H_3PO_5

The conversion ratio of H_3PO_5 based on H_2O_2 can be increased by increasing the mole ratio of P_2O_5:H_2O_2 (Fig. 2). When the mole ratio of P_2O_5:H_2O_2 is greater than 0.9, 100% conversion was achieved.

Effect of H_2O_2 concentration

The effect of H_2O_2 concentration on the preparation of H_3PO_5 is shown in Fig. 3. As expected, the concentration of H_2O_2 had a dramatic influence on the generation of H_3PO_5. Increasing the peroxide concentration decreases the amount

Fig. 2. Effect of increasing P_2O_5:H_2O_2 on the conversion of H_2O_2 to H_3PO_5 (70 wt % H_2O_2, 2°C, 120 min).

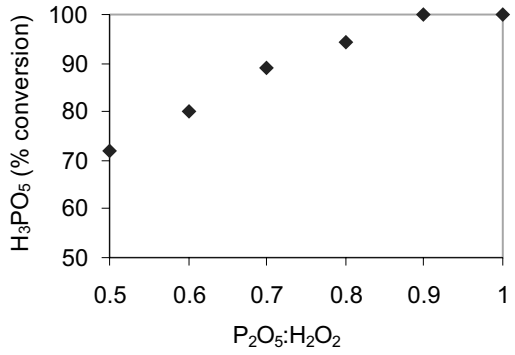
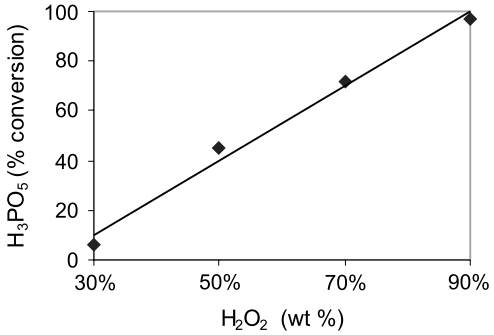


Fig. 3. Effect of H_2O_2 concentration on the conversion of H_2O_2 to H_3PO_5 (P_2O_5:H_2O_2 = 0.5:1, 2°C, 120 min).



of water available for the hydrolysis of P_2O_5 (eq. [7]). As a result, a higher percent of the H_2O_2 is converted into H_3PO_5. As can be seen from Fig. 3, 90 wt % H_2O_2 gave quantitative conversion. However, concerns exist regarding the safe handling of such highly concentrated H_2O_2 solutions. Therefore, the 70 wt % H_2O_2, which gave satisfactory results (>70% conversion), is a good compromise between H_2O_2 conversion and safe handling.

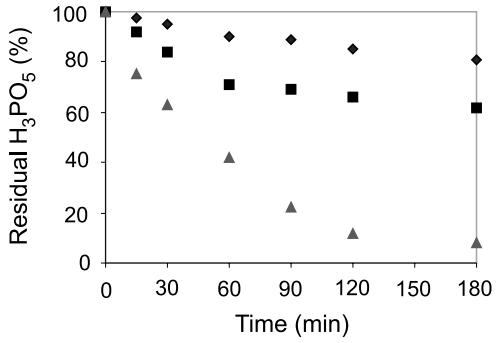
[7] $$P_2O_3 + 3H_2O \longrightarrow 2H_3PO_4$$

H_3PO_5 stability

To further characterize the peroxy acid synthesis, the stability of the respective peroxides was determined during the reaction process. Five reactions were conducted (P_2O_5:H_2O_2 (0.5:1), 2°C, 180 min), and the total peroxide species present was determined. Analysis of the aqueous solution, which contained H_3PO_5, H_2O_2, and H_3PO_4, showed a total peroxide concentration of 98.2 ± 0.5%. In fact, after 30 days of refrigeration (~5°C), more than 95% of the H_3PO_5 remained. Thus, any decomposition of the peroxide species during the preparation protocol or storage at low temperature is negligible. This remarkable stability provides the possibility that H_3PO_5 may not need to be generated on site when it is utilized in commercial processes.

The thermal stability at higher temperatures was also investigated. Figure 4 shows the effect of increasing temperature on H_3PO_5 stability. As expected, increasing the temperature from 50 to 90°C resulted in a dramatic decrease

Fig. 4. Effect of temperature on H_3PO_5 stability: ◆ 50°C, ■ 70°C, ▲ 90°C. Initial [H_3PO_5] = 0.100 M, [H_2O_2] = 0.0 M, pH = 1.02.



in H_3PO_5 stability. At 90°C more than 90% of the peroxy acid was decomposed within 120 min.

The decrease in H_3PO_5 concentration may be attributed to several factors, e.g., thermal- and (or) metal-catalyzed decomposition or aqueous hydrolysis. It is known that under acidic conditions in the presence of water peroxy acid hydrolysis takes place according to the equilibrium reaction present in eq. [8] (2).

[8] $$H_3PO_5 + H_2O \longrightarrow H_3PO_4 + H_2O_2$$

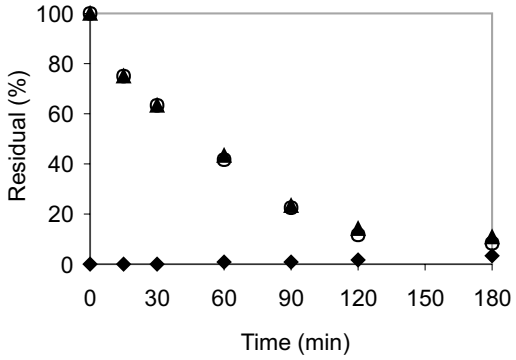
The hydrolysis of H_3PO_5 would result in the corresponding liberation of H_2O_2 and H_3PO_4. During the thermal treatments we monitored the concentration of H_3PO_5 and H_2O_2. Figure 5 shows the results obtained at 90°C.

It can be seen that very little H_2O_2 is generated during the 180 min of thermal treatment. However, this may be because of the thermal decomposition of the generated H_2O_2. To eliminate this possibility, H_2O_2 was thermally treated under the same reaction conditions (pH 1, 90°C), and no decomposition was observed. These results indicate that the rate of H_3PO_5 hydrolysis is extremely slow, and not responsible for the observed decrease in H_3PO_5 concentration under the conditions used. These results are in agreement with those of Battaglia and Edwards who reported that the hydrolysis of H_3PO_5 is negligible unless the pH is much less than 0 (16).

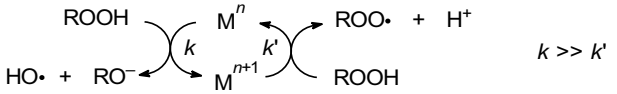
It is well established that peroxides undergo facile decomposition in the presence of transition metal ions. A kinetic chain reaction can be catalyzed by traces (10–20 ppm) of transition metal ions, particularly iron, cobalt, manganese, and copper, and is often referred to as Fenton's chemistry (2, 17). Under such conditions the peroxide acts as both a reducing and an oxidizing reagent with the transition metal ions in the higher and lower valence states, respectively (Scheme 1).

To minimize the effect of transition-metal-induced decomposition reactions, many techniques have been employed, which include the addition of sequestering agents and (or) inorganic salts to remove the majority of these metal ion contaminants (2, 18). To avoid the influence of trace amount of metal ions, which may be introduced during the preparation of H_3PO_5, the effect of DTPA on the reaction system was studied. Increasing concentrations of DTPA were used, and the effect on H_3PO_5 stability measured. There was no observable difference among any of the DTPA-included

Fig. 5. Decomposition of H_3PO_5 at 90°C: ◆ H_2O_2, ○ H_3PO_5, ▲ H_2O_2 + H_3PO_5. Initial [H_3PO_5] = 0.10 M, [H_2O_2] = 0.0 M, pH = 1.02.



Scheme 1.



reactions, and this indicates that metal-induced decomposition is not prevalent in our system.

Thermodynamically, peroxides, particularly peroxy acids, are potentially unstable, decomposing exothermically according to eq. [9].

[9] $$ROOH \xrightarrow{\Delta} ROH + 1/2\ O_2$$

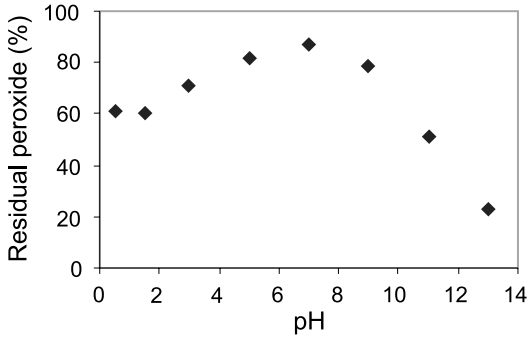
The facile decomposition is a result of the weak O—O bonds, ~31 kcal mol^{-1} for $CH_3C(O)O$—OH vs. 51 kcal mol^{-1} for HO—OH, which are easily cleaved by light and heat (2). In both peroxy acids and hydroperoxides, heating above a critical temperature (peracetic acid: ~80°C, H_2O_2: ~120°C (19)) initiates homolysis of the O—O bond, leading to the formation of radical species. What ensues is the kinetic decomposition of the peroxide to a variety of radical intermediates (2). Although we did not calculate the critical temperature for H_3PO_5, we are of the opinion that the decreased stability is mainly due to the thermal decomposition of H_3PO_5.

Finally, the effect of pH on the stability of H_3PO_5 (0.10 M) was studied at 70°C (Fig. 6). To avoid the influence of trace amounts of metal ions at high pH conditions where DTPA is not effective, DTMPA (0.1%) was added (20). The reaction was maintained at constant pH and temperature for 120 min, at which time the residual H_3PO_5 was determined. The results are shown in Fig. 6 and reveal that at approximately pH 7, H_3PO_5 has the maximum stability, which rapidly decreases with increasing pH.

Peracetic acid – peroxymonophosphoric acid preparation

To further increase the peroxy acid concentration of the reaction system, we investigated the effect of acetic acid addition. In previous studies, we found that the addition of acetic acid during peroxymonosulfuric acid synthesis results in an increase in peroxy acid concentration through the production of peracetic acid (21). In this system, the unreacted H_2O_2 reacts with the acetic acid to form peracetic acid, CH_3CO_3H, and the conversion ratio of the total peroxy acids

Fig. 6. Effect of pH on the stability of H_3PO_5 at 70°C and 120 min (initial [H_3PO_5] = 0.10 M).



based on H_2O_2 is increased. Therefore, glacial acetic acid was added to the P_2O_5–H_2O_2 reaction system prior to working up the reaction system (after approximately 2–3 h of reaction). The system was mixed for a further 30 to 45 min to promote CH_3CO_3H formation (21). The peroxy acids were then extracted from the CCl_4 layer and the concentration of peroxy acids and remaining hydrogen peroxide were determined by chemical methods. In a typical preparation, at a mole ratio of P_2O_2:H_2O_2:CH_3COOH = 0.5:1:0.3, using 70 wt % H_2O_2, the overall conversion ratio of H_2O_2 to peroxy acids was >95%.

Normally, the generation of peracetic acid from acetic acid and hydrogen peroxide requires a strong acid catalyst such as H_2SO_4. The advantage of this method is that no additional strong acid catalyst is needed, as H_3PO_4 and H_3PO_5 are both medium to strong acids. Although both acetic acid and peracetic acid are soluble in the CCl_4, they can be easily extracted by water at the end of the reaction. In fact, after 2–3 extractions (30 mL) with water, there was no acetic acid or peroxy acids left in the CCl_4. Thus, this system enables the CCl_4 to be reused, addressing some of the concerns surrounding its use.

Conclusions

In this paper we describe a new method for the preparation of peroxymonophosphoric acid (H_3PO_5). It utilizes a biphasic solution to moderate the vigorous reaction between phosphorous pentoxide (P_2O_5) and hydrogen peroxide (H_2O_2). Through careful control of the reaction temperature by the slow dropwise addition of H_2O_2, H_2O_2 can be converted to H_3PO_5 with high conversion ratios. Typical preparation conditions involve suspending the P_2O_5 in CCl_4, cooling the reaction system to 2°C, then slowly adding the 70 wt % H_2O_2 (P_2O_5:H_2O_2 = 0.5:1) while vigorously mixing the solution. The preparation is then left mixing at 2°C for between 120–180 min. Increasing the concentration of H_2O_2 as well as the mole ratio of P_2O_5:H_2O_2 leads to a higher % conversion of H_2O_2 to H_3PO_5. The addition of glacial acetic acid to the P_2O_5:H_2O_2 suspension at the end of the 120–180 min reaction (P_2O_5:H_2O_2:CH_3COOH = 0.5:1:0.3) leads to the formation of peracetic acid in addition to H_3PO_5 and an overall increase in the conversion ratio of total peroxy acids based on H_2O_2 (>95%).

The H_3PO_5 solution can be stored for more than 30 days under refrigeration with only minimal loss in H_3PO_5 concen-

tration. Temperature and pH have dramatic effects on the H_3PO_5 stability. At high temperature (70°C), the maximum H_3PO_5 stability was observed at a pH ~7, with both increasing and decreasing pH resulting in a decrease in residual H_3PO_5 after 120 min. Increasing the temperature to 90°C lead to the rapid reduction in H_3PO_5 concentration. Experimental results indicate that aqueous mediated hydrolysis and transition-metal-catalyzed decomposition are not prevalent. The observed decrease in H_3PO_5 can be attributed to the thermal homolysis of the peroxygen bond.

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