Chapter 3

Synthesis, Characterisation, and Reactivity of Sodium and Ammonium Peroxomonophosphate Trihydrates, \( A_3 \left[ \text{PO}_3 (\text{O}_2) \right] \cdot 3\text{H}_2\text{O} \) 
\((A = \text{Na or } \text{NH}_4)\)

and

First Chemical Synthesis of a Fluorinated Peroxophosphate:
Ammonium Peroxo(fluoro)monophosphate Dihydrate, 
\((\text{NH}_4)_2 \left[ \text{PO}_2 (\text{O}_2) \text{F} \right] \cdot 2\text{H}_2\text{O}^*\)

A perusal of the literature pertaining peroxo-element chemistry reveals that studies on non-metal peroxo compounds has not received due attention, and comparatively a very little is reported about non-metal peroxo species. Some peroxo-compounds of non-metals like peroxodicarbonates,\(^1\) peroxomonocarbonates,\(^1\) peroxodisulphates,\(^2,3\) peroxomonosulphates,\(^4,5\) peroxodiphosphates\(^6\) and peroxomonophosphoric acid\(^6\) are known and are widely used in laboratory as well as in industry, but synthetic routes to many of these compounds are not straight forward. For example,

\*A part of the work described in this Chapter has been published: J. Chem. Soc., Dalton Trans., 1988, 2005;

Another part of the work has been accepted for publication: Proceedings of I World Congress II European Workshop Symposium in "New Developments in Selective Oxidation," Rimini, Italy, 1989.
phosphorous is known to form compounds with peroxide, but only a little is known regarding this aspect of phosphorous chemistry. The most well documented among peroxo-phosphorous compounds are peroxomonophosphoric acid in solution and peroxodiphosphates, $A_4P_2O_8$ ($A = \text{Na, NH}_4$ or K) in addition to a poorly characterised unstable peroxide, $P_2O_6$, and a diperoxophosphate. Between the two categories namely peroxomonophosphoric acid and peroxodiphosphates, the latter ones are rather well characterised.

Although the importance of peroxomonophosphoric acid has been highlighted in the literature, it is not very easy to obtain. Further, free peroxomonophosphoric acid does not permit an easy isolation. Peroxomonophosphoric acid came into existence with the first report of its synthesis in 1910 and since then various techniques for its preparation and results of studies of decomposition mechanism and dissociation constants have been reported. A scrutiny of the reported methods for generation of the acid shows that while some of the methods afford an impure product, the others are capable of producing a pure 2M solution of peroxomonophosphoric acid. However, the latter methods require highly concentrated hydrogen peroxide (80-95%) that is not very commonly available, thus limiting its accessibility. It is noteworthy that no salt of the $\text{PO}_3(O_2)^-$ ion, but for an acid salt $\text{KH}_2\text{PO}_3(O_2)^-$, is reported. The salt, $\text{KH}_2\text{PO}_3(O_2)^-$ has been prepared from the reaction of $\text{P}_4\text{O}_{10}$ with 84% $\text{H}_2\text{O}_2$ in the presence of 43% KOH solution by conducting the reaction in a perhalogenated solvent.
Despite the difficulties in obtaining permonophosphoric acid, it has drawn quite a lot of attention especially because of its versatile oxidising potentialities.

In view of the above mentioned interesting and very useful properties of peroxomonophosphoric acid, although it is difficult to obtain, it was considered essential to synthesise the salts of the acid and explore their properties particularly in terms of their reactivity. This was also anticipated to be a rewarding area of investigation and might lead to an easy access to the peroxo-phosphorous chemistry.

Over and above what has been stated, hetero-ligand peroxo compounds of non-metals in general, and of phosphorous in particular, is very poorly investigated. It was reported over a half-a-century ago\textsuperscript{26} that anodic oxidations of fluorophosphoric acids produced peroxo(fluoro)phosphoric acids, $\text{H}_2\text{PO}_2(\text{O}_2)\text{F}$ and $\text{H}_2\text{P}_2\text{O}_4(\text{O}_2)\text{F}_2$, only in ca.2% yields. The compounds are poorly characterised and to our knowledge neither any salts of the acid nor any chemical synthesis of fluorinated peroxophosphate is reported until date. In addition to simple peroxophosphates, we also sought to develop a route to chemical synthesis of fluorinated peroxophosphate followed by studies of reactivity of such species.

Accordingly, studies on peroxo- and fluorinated peroxo-phosphates were undertaken. The present Chapter of the thesis describes a very simple and efficient method of synthesis along with structural assessment of heretofore unreported ammonium
and sodium peroxomonophosphate trihydrates, $A_3\left[PO_3(O_2)\right]_3\cdot 3H_2O$ ($A = \text{Na or NH}_4$), which are as efficacious as the acid with some added advantages. We also report herein the results of our studies of reactivity of the compounds. This Chapter also describes a simple chemical synthesis of hitherto unknown ammonium peroxo-(fluoro)phosphate dihydrate, $(\text{NH}_4)_2\left[PO_2(O_2)\right]_2\cdot 2H_2O$, the first chemically synthesised peroxo(fluoro)phosphate, along with its structural assessment, and some results of our studies of its reactivity with inorganic as well as organic substrates.

**Experimental**

All chemicals used were reagent grade products (E. Merck, BDH, Sarabhai M. Chemicals, SISCO).

**Synthesis of Ammonium and Sodium Peroxomonophosphate Trihydrates, $A_3\left[PO_3(O_2)\right]_3\cdot 3H_2O$ ($A = \text{NH}_4, \text{Na}$)**

In a typical procedure, disodium or diammonium hydrogen phosphate, $A_2HPO_4$ ($A = \text{NH}_4$ or Na) (7.57 mmol) was dissolved in 15 cm$^3$ (132.3 mmol) of 30% $H_2O_2$. The reaction solution was stirred for ca. 15 min. followed by slow addition of aqueous ammonia (sp. gr. 0.9) or a 20% solution of sodium hydroxide in the cases of ammonium and sodium salts, respectively, until the pH of the reaction mixture was found to be 9.5. An amount of 50 cm$^3$ of 95% ethanol was added to the reaction solution with continuous stirring. An oily mass separated out at this stage.
The reaction mixture was stirred further for ca 20 min. and allowed to stand for one hour. The supernatent liquid was decanted off and the oily mass was treated repeatedly with ethanol until white crystalline \( \text{Na}_3 \left( \text{PO}_3 (\text{O}_2) \right) \cdot 3\text{H}_2\text{O} \) or \( \text{(NH}_4)_3 \left( \text{PO}_3 (\text{O}_2) \right) \cdot 3\text{H}_2\text{O} \) was obtained. The compound was separated by filtration in a suction, washed 4-5 times with ethanol, and finally dried in vacuo over concentrated \( \text{H}_2\text{SO}_4 \).

The amount of reagents used and the yields of the compounds obtained are set out in Table 3.1.

Studies of Reactivity of Sodium Peroxomonophosphate Trihydrate, \( \text{Na}_3 \left( \text{PO}_3 (\text{O}_2) \right) \cdot 3\text{H}_2\text{O} \)

Starting Material

Commercially available pure samples of various alcohols, benzonitrile, salicylaldehyde, and anthracene were used. The compounds were purified before use.

Two \( \alpha, \beta \)-unsaturated ketones e.g., benzylidene acetophenone and benzylidene 4'-methoxy acetophenone were prepared by reported procedures, and their purity checked by comparing melting points and spectra with those of the reported ones.

All the following oxidation reactions were conducted under pure \( \text{N}_2 \) atmosphere.
Table 3.1: Amounts of Reagents Used and the Yields of Ammonium and Sodium Peroxomonophosphate Trihydrates, $A_3 \left[PO_3(O_2)\right] \cdot 3H_2O$ ($A = NH_4$ or Na)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$A_2HPO_4$ g (mmol)</th>
<th>Amount of $30% H_2O_2$ cm$^3$ (mmol)</th>
<th>Yield g (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>($NH_4)_3 \left[PO_3(O_2)\right] \cdot 3H_2O</td>
<td>1 (7.57)</td>
<td>15 (132.3)</td>
<td>1.6 (96)</td>
</tr>
<tr>
<td>$Na_3 \left[PO_3(O_2)\right] \cdot 3H_2O</td>
<td>1.1 (7.57)</td>
<td>15 (132.3)</td>
<td>1.6 (90)</td>
</tr>
</tbody>
</table>
(i) Reactions of Chalcones with Sodium Peroxomonophosphate Trihydrate, \( \text{Na}_3 \left[ \text{PO}_3 (\text{O}_2) \right] \cdot 3\text{H}_2\text{O} \)

A 4.81 mmol sample of the chalcone was dissolved in 25 cm\(^3\) of THF. To the above solution was added an aqueous solution (25 cm\(^3\)) of \( \text{Na}_3 \left[ \text{PO}_3 (\text{O}_2) \right] \cdot 3\text{H}_2\text{O} \) (1.69g; 7.23 mmol) drop by drop, from a dropping funnel, over a period of 20-30 min with continuous stirring at room temperature. The stirring was continued for a further period of two hours. The reaction solution was then poured on to 100 cm\(^3\) of water containing crushed ice. The crude chalcone epoxide separates out at this stage. The mixture was stirred for 15 min and then filtered off under suction and washed 4-5 times with cold water, dried, and recrystallised from methanol.

The amount of reagent used and the yields and melting points of the products obtained are given in Table 3.2. The IR and NMR spectra were found to be superimposable with those reported in the literature.\(^{27}\)

(ii) Reaction of Salicylaldehyde with Sodium Peroxomonophosphate Trihydrate, \( \text{Na}_3 \left[ \text{PO}_3 (\text{O}_2) \right] \cdot 3\text{H}_2\text{O} \)

To a 1.0g (8.27 mmol) sample of salicylaldehyde an aqueous solution (25 cm\(^3\)) of \( \text{Na}_3 \left[ \text{PO}_3 (\text{O}_2) \right] \cdot 3\text{H}_2\text{O} \) (2.9g; 12.40 mmol) was added with stirring. The solution temperature rose spontaneously to ca. 60°C and a dark colour developed. The reaction solution was stirred for 8h and then allowed to stand overnight. The solution was neutralised with acetic acid,
evaporated to dryness, and the residue was treated with toluene 
(5 x 10 cm$^3$). The toluene fraction was dried (Na$_2$SO$_4$) and upon 
evaporation gave catechol. The crude catechol thus obtained was 
purified by passing through a silica gel column using hexane/ 
ethylacetate (6:4) as the eluent.

The amount of reagent used and the yield of the product 
obtained and its melting point are reported in Table 3.2. The 
IR and NMR spectra were compared with those of the reported 
ones$^{28}$ and found to be superimposable.

(iii) Reaction of Benzonitrile with Na$_3$PO$_3$(O$_2$)$_7$·3H$_2$O

Benzonitrile (1.0g, 9.71 mmol) was mixed with 15 cm$^3$ of 
ethanol and to this was added an aqueous solution (30 cm$^3$) of 
Na$_3$PO$_3$(O$_2$)$_7$·3H$_2$O (6.8g; 29.07 mmol). The reaction solution 
was stirred for 3h at ca. 50°C on an oil-bath. The reaction 
solution was cooled to room temperature and treated with 
chloroform (3 x 15 cm$^3$). Combined organic layers were washed 
with water (1 x 50 cm$^3$), dried (Na$_2$SO$_4$), and concentrated to 
give crude benzamide which was purified by recrystallisation 
from chloroform.

Amount of reagent used and the yield and melting of the 
product are set out in Table 3.2. The IR and NMR spectral position 
are found to be similar to those of an authentic sample.

(iv) Reaction of Na$_3$PO$_3$(O$_2$)$_7$·3H$_2$O with Benzil

An acetonitrile (15 cm$^3$) solution of benzil (1.0g, 4.76 mmol) 
was mixed with an aqueous solution (30 cm$^3$) of Na$_3$PO$_3$(O$_2$)$_7$·3H$_2$O
(1.67g; 7.14 mmol) and the mixture was refluxed for ca. 1h. The reaction mixture was poured to ice-cold water (50 cm³) after cooling to room temperature. Unreacted benzil came out as a yellow solid which was filtered and washed with water (2-3 times). The combined filtrate and washings was acidified with hydrochloric acid and then treated with chloroform (4 x 20 cm³). The combined organic layers were washed with water (1 x 10 cm³), dried (Na₂SO₄), and concentrated to obtain benzoic acid. The crude product was purified by recrystallisation from chloroform.

The yield and melting point of the oxidised product as well as the amount of reagent used for the oxidation are included in Table 3.2. The IR spectrum was found to be superimposable with that of an authentic sample.

(v) Reaction of Na₃[PO₃(O₂)₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋ śmiercię wiersza antracenu (1.0g; 5.62 mmol) and acetic acid (30 cm³) were placed in a flask and the whole was refluxed until the whole amount of anthracene went into solution. An aqueous solution (15 cm³) of Na₃[PO₃(O₂)₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Amount of Substrate g (mmol)</th>
<th>Amount of $\text{Na}_3\left[\text{PO}_3\left(\text{O}_2\right)_2\right] \cdot 3\text{H}_2\text{O}$ g (mmol)</th>
<th>Product</th>
<th>Yields g (mmol) (%)</th>
<th>m.p. (Uncorrected) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyldiene acetophenone</td>
<td>1.0 (4.81)</td>
<td>1.69 (7.22)</td>
<td>Epoxide</td>
<td>0.8 (74)</td>
<td>90</td>
</tr>
<tr>
<td>Benzyldiene p-methoxy acetophenone</td>
<td>1.0 (4.20)</td>
<td>1.47 (6.28)</td>
<td>Epoxide</td>
<td>0.9 (84)</td>
<td>79</td>
</tr>
<tr>
<td>Salicylaldehyde</td>
<td>1.0 (8.19)</td>
<td>2.9 (12.40)</td>
<td>Catechol</td>
<td>0.8 (88)</td>
<td>103</td>
</tr>
<tr>
<td>Benzonitrile</td>
<td>1.0 (9.70)</td>
<td>6.8 (29.06)</td>
<td>Benzamide</td>
<td>0.9 (76)</td>
<td>128</td>
</tr>
<tr>
<td>Benzil</td>
<td>1.0 (4.76)</td>
<td>1.67 (7.14)</td>
<td>Benzoic acid</td>
<td>0.5 (43)</td>
<td>122</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.0 (5.61)</td>
<td>1.97 (8.42)</td>
<td>Anthraquinone</td>
<td>0.70 (60)</td>
<td>284</td>
</tr>
</tbody>
</table>
thus obtained was purified by passing through a silica gel column using hexane/ethylacetate (9:1) as the eluent. The yield and melting point of the product, and amount of reagent used are presented in Table 3.2. The NMR and IR spectra compare very well with those of an authentic sample.

(vi) Reaction of $\text{Na}_3\text{PO}_3\text{(O}_2\text{)}\text{H}_2\text{O}$ with Alcohols.

A General Procedure

In a typical procedure the alcohol was mixed with ca. 20 cm$^3$ of water and to it was added 1.5 cm$^3$ of concentrated $\text{H}_2\text{SO}_4$. To the above reaction mixture was added a solid sample of $\text{Na}_3\text{PO}_3\text{(O}_2\text{)}\text{H}_2\text{O}$ maintaining the ratio of alcohol : $\text{PO}_5^-$ as 1:1.5. The reaction mixture was refluxed for 1h and then cooled to room temperature followed by neutralisation with $\text{NaHCO}_3$. The aldehyde or ketone was isolated as its 2,4-dinitrophenyl hydrazine derivative from which the yields of the carbonyl compounds were calculated. The amount of reagent used and the yields of the products and the melting points of their 2,4-dinitro-phenyl hydrazine derivatives are summarised in Table 3.3.

Synthesis of Ammonium Peroxo(fluoro)monophosphate Dihydrate, $(\text{NH}_4)_2\text{PO}_2\text{(O}_2\text{)F}\text{H}_2\text{O}$

A mixture of 1.0g (8.69 mmol) ammonium dihydrogen-phosphate, $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, and 1 cm$^3$ (24 mmol) of 48% HF was allowed to react with 15 cm$^3$ (132.3 mmol) of 30% hydrogen peroxide in an ice-bath, at pH 10-11 held by a careful addition of aqueous
Table 3.3: Amounts of the Reagent Used and Yields and Melting Points of 2,4-dinitrophenyl hydrazine Derivatives of Oxidation Products of Alcohols. The reagent used was Na₃PO₃(O₂).₃H₂O

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Amount of Alcohol (g (mmol))</th>
<th>Amount of Na₃PO₃(O₂).₃H₂O (g (mmol))</th>
<th>Product</th>
<th>Yield (%)</th>
<th>m.p. of 2,4-dinitrophenyl hydrazine °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Propanol</td>
<td>2.0 (33.27)</td>
<td>11.7 (50.01)</td>
<td>Propionaldehyde</td>
<td>34</td>
<td>153 - 154</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>2.0 (26.98)</td>
<td>9.61 (41.08)</td>
<td>Butaldehyde</td>
<td>36</td>
<td>122 - 123</td>
</tr>
<tr>
<td>iso-Butanol</td>
<td>2.0 (26.98)</td>
<td>9.48 (40.52)</td>
<td>isobutaldehyde</td>
<td>37</td>
<td>187 - 188</td>
</tr>
<tr>
<td>iso-Propanol</td>
<td>2.0 (33.27)</td>
<td>11.7 (50.01)</td>
<td>Acetone</td>
<td>40</td>
<td>127 - 128</td>
</tr>
</tbody>
</table>
ammonia (sp. gr. 0.9) with stirring. Stirring was continued for a further period ca. 7 min followed by the addition of ca. 25 cm$^3$ of ice-cold ethanol whereupon white crystalline ammonium peroxo-(fluoro)monophosphate dihydrate, \((\text{NH}_4)_2 \overline{\text{PO}_2(N\text{O}_2)F\cdot2\text{H}_2\text{O}} \) was precipitated. This was separated by filtration, washed 5-6 times with ethanol, and finally dried in vacuo over concentrated \(\text{H}_2\text{SO}_4\). The yield of \((\text{NH}_4)_2 \overline{\text{PO}_2(N\text{O}_2)F\cdot2\text{H}_2\text{O}} \) was 1.3g (81%).

**Studies of Reactivity of Ammonium Peroxo(fluoro)monophosphate Dihydrate,** \((\text{NH}_4)_2 \overline{\text{PO}_2(N\text{O}_2)F\cdot2\text{H}_2\text{O}} \)

**Starting Materials**

Commercially available pure samples of the various alcohols viz. n-propanol, n-butanol, and isopropanol, styrene and anthracene were used. The compounds were purified before use. Cyclohexene was prepared by the reported method$^{29}$ and its identity was confirmed by comparing its IR and NMR spectra with those of the reported ones.$^{30}$

\(\text{SO}_2(g)\) was generated from the reaction of copper turnings with concentrated sulphuric acid.

(1) **Reaction of \((\text{NH}_4)_2 \overline{\text{PO}_2(N\text{O}_2)F\cdot2\text{H}_2\text{O}} \) with Cyclohexene**

A 2.0g (24.39 mmol) sample of cyclohexene and 25 cm$^3$ of 80% formic acid were placed in a round bottomed flask. To it was added solid \((\text{NH}_4)_2 \overline{\text{PO}_2(N\text{O}_2)F\cdot2\text{H}_2\text{O}}\) (6.81g; 36.60 mmol). The reaction mixture was stirred magnetically at room temperature for 3h. The mixture was then neutralised with \(\text{NaHCO}_3\) and
Table 3.4: Amounts of the Reagent Used and Yields and Melting Points of the Reaction Products. The Reagent Used was \((NH_4)_2PO_2(O_2)F\cdot2H_2O\).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Amount of Substrate g (mmol)</th>
<th>Amount of ((NH_4)_2PO_2(O_2)F\cdot2H_2O) g (mmol)</th>
<th>Product</th>
<th>Yield g (%)</th>
<th>m.p. (Uncorrected) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene</td>
<td>2.0 (24.39)</td>
<td>6.81 (36.6)</td>
<td>Trans 1,2-cyclohexanediol</td>
<td>0.7 (49)</td>
<td>102-103</td>
</tr>
<tr>
<td>Styrene</td>
<td>2.0 (19.20)</td>
<td>5.37 (28.66)</td>
<td>1-Phenylethylene-glycol</td>
<td>0.5 (38)</td>
<td>66 - 68</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.0 (5.62)</td>
<td>1.57 (8.44)</td>
<td>Anthraquinone</td>
<td>0.8 (68)</td>
<td>284</td>
</tr>
</tbody>
</table>
treated with chloroform (4 x 20 cm³). The extract was washed with water (1 x 20 cm³), dried by treating with Na₂SO₄, and then concentrated to afford white crystalline 1,2-cyclohexanediol. The product was purified by passing through a column using hexane/ethylacetate (6:4) as the eluent.

The amount of reagent used for the oxidation and the yield of the product along with its melting point are reported in Table 3.4. The IR and NMR spectra compare very well with those of an authentic sample.

(ii) Reaction of (NH₄)₂PO₂(O₂)F⁻, 2H₂O with Styrene

The reaction of styrene with ammonium peroxo(fluoro)monophosphate, (NH₄)₂PO₂(O₂)F⁻, 2H₂O, was carried out in a similar manner as described under the reaction of cyclohexene. The end product was found to be 1-phenyl ethyleneglycol.

The yield and melting point of the product, and the amount of reagent used for the oxidation are given in Table 3.4. The IR and NMR spectra were found to be similar to those of a standard sample.

(iii) Reaction of (NH₄)₂PO₂(O₂)F⁻, 2H₂O with Alcohols.

A representative method

In a typical procedure the alcohol was reacted with (NH₄)₂PO₂(O₂)F⁻, 2H₂O in a manner analogous to that described under the reaction of sodium peroxomonophosphate trihydrate, Na₃PO₃(O₂)⁻, 3H₂O, with alcohols.
Table 3.5: Amounts of the Reagent Used and Yields and Melting Points of 2,4-dinitrophenylhydrazine Derivatives of the Oxidation Products of Alcohols

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Amount of Alcohol g (mmol)</th>
<th>Amount of (NH₄)₂PO₂(O₂)F·₂H₂O g (mmol)</th>
<th>Product</th>
<th>Yield %</th>
<th>m.p. of 2,4-dinitrophenyl hydrazone °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Propanol</td>
<td>2.0 (33.27)</td>
<td>9.3 (49.99)</td>
<td>Propionaldehyde</td>
<td>38</td>
<td>154 - 155</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>2.9 (26.98)</td>
<td>7.54 (40.53)</td>
<td>Butaldehyde</td>
<td>39</td>
<td>122 - 123</td>
</tr>
<tr>
<td>iso-Propanol</td>
<td>2.0 (33.27)</td>
<td>9.3 (49.99)</td>
<td>Acetone</td>
<td>41</td>
<td>127 - 128</td>
</tr>
</tbody>
</table>
The amount of reagents used and the yields of the products and melting points of the 2,4-dinitrophenylhydrazine derivatives are incorporated in Table 3.5.

(iv) Reaction of \((\text{NH}_4)_2 \text{PO}_2(\text{O}_2)\text{F} \cdot 2\text{H}_2\text{O}\) with Anthracene

The reaction of anthracene with \((\text{NH}_4)_2 \text{PO}_2(\text{O}_2)\text{F} \cdot 2\text{H}_2\text{O}\) was carried out in a similar way as that described under the reaction of \(\text{Na}_3 \text{PO}_3(\text{O}_2) \cdot 3\text{H}_2\text{O}\) with anthracene. The product anthraquinone was isolated and purified in a similar fashion as already described. The compound was characterised by melting point determination and spectral measurements followed by comparison of the results with those of an authentic sample.

The amount of reagent used and the yield of the product are given in Table 3.4.

(v) Reaction of \((\text{NH}_4)_2 \text{PO}_2(\text{O}_2)\text{F} \cdot 2\text{H}_2\text{O}\) with \(\text{SO}_2(\text{g})\)

The water used for the reaction was deoxygenated by the following procedure. The water sample was first boiled for \(\text{ca.} 30\) min under \(\text{N}_2\) atmosphere and it was cooled to room temperature. This was followed by bubbling of \(\text{N}_2\) gas through it for a period of \(\text{ca.} 15\) min. The deoxygenated water thus obtained was stored in an air tight container.

Through an aqueous solution (15 cm\(^3\)) of 1.0g (5.4 mmol) of ammonium peroxo(fluoro)monophosphate, \((\text{NH}_4)_2 \text{PO}_2(\text{O}_2)\text{F} \cdot 2\text{H}_2\text{O}\), \(\text{SO}_2(\text{g})\) was bubbled for about 15 min with occasional stirring. The bubbling of \(\text{SO}_2(\text{g})\) was stopped and the reaction solution was
allowed to stand at room temperature. Ethanol (95%) was added to the solution to just initiate precipitation and then left for ca. 2h whereupon white crystalline ammonium sulphate separated. This was filtered, washed 2-3 times with ethanol, and finally dried in vacuo over concentrated H₂SO₄. The product was identified as ammonium sulphate, (NH₄)₂SO₄, by chemical analyses and IR spectroscopy.³¹

**Elemental Analyses**

Quantitative estimation of peroxide, fluoride, phosphorous, nitrogen, and sodium were made by the methods described in Chapter 2. The analytical data and molar conductance values are reported in Table 3.6 and Table 3.8.

---

**Results and Discussion**

**Ammonium and Sodium Peroxomonophosphate Trihydrate,**

A₃[PO₃(O₂)]⁻·3H₂O (A = NH₄, Na). Synthesis, Characterisation, and an Assessment of Structure

It was reported by Schmidlin and co-workers²¹ that an interaction of 30% H₂O₂ solution with P₄O₁₀ produced permonophosphoric acid in solution. Subsequently it was shown¹⁹ that the product so obtained was a crude one, and any attempt to prepare the salts of the acid failed. Later on various improvised techniques for its preparation were developed¹⁹,²² but no salt, except an acid salt, KH₂PO₅, could be synthesised. All the improvised routes to permonophosphoric acid referred to above¹⁹,²² required
80-90% $H_2O_2$. The use of such highly concentrated $H_2O_2$ solutions need a very careful handling and manipulations causing a restricted accessibility of the desired species.

From the experience gathered in the laboratory, where the present investigation was carried out, in the field of peroxo-element chemistry, it was anticipated that reactions of appropriate salts of phosphoric acid with 30% $H_2O_2$ under suitable experimental conditions might lead to the synthesis of salts of peroxomonophosphoric acid. It has also been established from a number of experiments that one of the most important parameters in successful synthesis is a conducive pH of the reaction solution.

Accordingly, successful synthesis of the title compounds was achieved from a reaction of the di-ammonium or di-sodium hydrogen phosphate with 30% $H_2O_2$ at pH 9.5 held by the addition of aqueous ammonia (sp. gr. 0.9) or 20% sodium hydroxide solution.

$$A_2HPO_4 + H_2O_2 + AOH \rightarrow A_3 \left(PO_3(O_2)_2\right) + 2H_2O$$

$(A = NH_4 \text{ or } Na)$

the role of alkali was not only to facilitate peroxygenation but also to act as a source of counter cations, while ethanol helped in precipitation of the product.

The compounds have been obtained as white crystalline products and can be stored for a prolonged period in sealed containers at a freezer temperature without decomposition. At room temperature, however, the compounds can be stored undecomposed in vacuo only for a day or so. The stability of the
compounds can be ascertained by quantitative estimation of active oxygen content at a regular interval. The compounds are insoluble in common organic solvents but are highly soluble in water. The molar conductance measurements gave a value of 327-340 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ in conformity with their 3:1 electrolytic nature. The aqueous solutions of the compounds are found to be basic in nature $\text{pH}$ of 0.01M solution of $\text{Na}_3 \left[\text{PO}_3(O_2)\right] \cdot 3\text{H}_2\text{O} = 8.9$; $\text{pH}$ of 0.01M solution of $(\text{NH}_4)_3 \left[\text{PO}_3(O_2)\right] \cdot 3\text{H}_2\text{O} = 7.9$ and this is explained in terms of hydrolysis of the salts in an aqueous medium. This further suggests that peroxomonophosphoric acid is a relatively weak acid and thus an aqueous solution of its salt reacts basic. This property of the compounds is very important particularly in the context of their reactivity (as shown latter in this section). The product decompose in an acidic solution (dil. H$_2$SO$_4$) quantitatively liberating H$_2$O$_2$ and rendering it easy to estimate the active oxygen contents. The peroxide contents have been determined by redox titrations separately involving a standard KMnO$_4$ solution or a standard Ce$^{4+}$ solution. The results of peroxide estimation, and those of elemental analyses for the counter cation and phosphorous show the stoichiometry of $A: P: O_2^{2-}$ (active oxygen) to be 3:1:1 (Table 3.6) in complete agreement with their formulae, $A_3 \left[\text{PO}_3(O_2)\right] \cdot 3\text{H}_2\text{O}$ ($A = \text{NH}_4$ or Na).

The vibrational spectra of the compounds show bands due to the presence of coordinated peroxide ($O_2^{2-}$), $33 (\text{PO}_3)^{34}$ and
Table 3.6: Analytical Results and Molar Conductance Values of Ammonium and Sodium Peroxomonophosphate Trihydrates, $A_3 \left[PO_3(O_2)\right]_{3H_2O} (A = NH_4, Na)$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molar Conductance $\Omega^{-1} cm^2 mol^{-1}$</th>
<th>Found % (Calcd. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(NH_4)<em>3 \left[PO_3(O_2)\right]</em>{3H_2O}$</td>
<td>330</td>
<td>Na or N</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$O_A^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19.1 (19.18)</td>
</tr>
<tr>
<td>$Na_3 \left[PO_3(O_2)\right]_{3H_2O}$</td>
<td>340</td>
<td>29.1 (29.49)</td>
</tr>
</tbody>
</table>

$^a$Active Oxygen
lattice water. The presence of lattice water is clearly evidenced by the IR bands at ca. 3400 cm\(^{-1}\) due to \(\nu (O-H)\) and at ca. 1650 cm\(^{-1}\) due to \(\delta (H-O-H)\). There has been no indication for the occurrence of \(H_2O_2\) of crystallisation. The presence of \(PO_3\) moiety is clearly reflected in the IR spectra from the display of wide splitting of the \((PO_3)\) stretching and deformation modes. Thus the bands at ca. 1070, 1130, 1140 cm\(^{-1}\) have been assigned to \(\nu_{as} (PO_3)\) while those at ca. 950s and 1000s cm\(^{-1}\) have been attributed to \(\nu_s (PO_3)\) (Table 3.7). The peroxo stretching mode \(\nu (O-O)\) appears at ca. 870 cm\(^{-1}\). The frequencies at ca. 510, ca. 540, and at ca. 570 cm\(^{-1}\) have been assigned to \(\delta (PO_3)\) modes. The laser Raman (IR) spectra of the newly synthesised peroxo-phosphates show complementary signals at ca. 1078, ca. 1155, and ca. 1189 cm\(^{-1}\) due to \(\nu_{as} (PO_3)\), at ca. 990 and ca. 950 cm\(^{-1}\) due to \(\nu_s (PO_3)\). The laser Raman (IR) signals at ca. 872 cm\(^{-1}\) complements the corresponding IR signal which owe their origin to \(\nu (O-O)\) mode of the bonded peroxide. The IR signals at ca. 530 and 476 cm\(^{-1}\) have been attributed to \(\delta (PO_3)\) modes. The IR and laser Raman spectra totally conform to the formulations of the compounds as \(A_3\sum_{\bigwedge_{\nu O_2} 3H_2O}\) with the peroxide \((O_2^{2-})\) group being presumably bonded in an end-on manner as often encountered in simple monoperoxo derivatives of other elements namely sulphur and carbon.

Reactivity of Sodium Peroxomonophosphate Trihydrate, 

\[Na_3\sum_{\bigwedge_{\nu O_2} 3H_2O}\]

As mentioned earlier in this section that aqueous solutions of the peroxomonophosphates react basic with the pH values lying
Table 3.7: Structurally Significant IR and Raman Bands of Ammonium and Sodium Peroxomonophosphate Trihydrates, $A_3 \left[PO_3(O_2)\right]_3 H_2 O$ ($A = NH_4$ or Na)

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR $cm^{-1}$</th>
<th>Raman $cm^{-1}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(NH_4)_3 \left[PO_3(O_2)\right]_3 H_2 O$</td>
<td>1070s</td>
<td>1070</td>
<td>$\nu_{as}(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>1110s</td>
<td>1150</td>
<td>$\nu_{as}(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>1160s</td>
<td>1160</td>
<td>$\nu_{as}(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>950s</td>
<td>940</td>
<td>$\nu_{s}(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>1000s</td>
<td>990</td>
<td>$\nu_{s}(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>430m</td>
<td>470</td>
<td>$\delta(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>530s</td>
<td>530</td>
<td>$\delta(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>560s</td>
<td>530</td>
<td>$\delta(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>890s</td>
<td>880</td>
<td>$\nu(O-O)$</td>
</tr>
<tr>
<td></td>
<td>1660m</td>
<td>880</td>
<td>$\nu(O-H)$</td>
</tr>
<tr>
<td></td>
<td>3400s</td>
<td>880</td>
<td>$\nu(O-H)$</td>
</tr>
<tr>
<td></td>
<td>1400s</td>
<td>3050s</td>
<td>$\nu_4$ of $N-H$ modes</td>
</tr>
<tr>
<td></td>
<td>3160m</td>
<td>3160m</td>
<td>$\nu_1$ of $N-H$ modes</td>
</tr>
<tr>
<td></td>
<td>3160m</td>
<td>3160m</td>
<td>$\nu_3$ of $N-H$ modes</td>
</tr>
<tr>
<td>$Na_3 \left[PO_3(O_2)\right]_3 H_2 O$</td>
<td>1070s</td>
<td>1078</td>
<td>$\nu_{as}(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>1130s</td>
<td>1155</td>
<td>$\nu_{as}(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>1140s</td>
<td>1189</td>
<td>$\nu_{as}(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>960s</td>
<td>952</td>
<td>$\nu_{s}(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>990s</td>
<td>986</td>
<td>$\nu_{s}(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>510s</td>
<td>476</td>
<td>$\delta(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>540m</td>
<td>530</td>
<td>$\delta(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>570m</td>
<td>530</td>
<td>$\delta(PO_3)$</td>
</tr>
<tr>
<td></td>
<td>870s</td>
<td>875</td>
<td>$\nu(O-O)$</td>
</tr>
<tr>
<td></td>
<td>1650m</td>
<td>875</td>
<td>$\nu(O-H)$</td>
</tr>
<tr>
<td></td>
<td>3400s</td>
<td>875</td>
<td>$\nu(O-H)$</td>
</tr>
</tbody>
</table>
\[ (\text{NH}_4)_3\{\text{PO}_3\{\text{O}_2\}\} \cdot 3\text{H}_2\text{O} \]

\[ \text{Na}_3\{\text{PO}_3\{\text{O}_2\}\} \cdot 3\text{H}_2\text{O} \]
\[
\kappa = 4880 \text{ Å}
\]
between 8 and 9 (0.01M solutions). This particular property of the compounds was quite intriguing because it led us to anticipate that the compounds might be capable of being used as viable substitutes for the basic-\(\text{H}_2\text{O}_2\) reagent with some added advantages e.g. easy to handle and to maintain stoichiometry.

Typically, \(\alpha, \beta\) -unsaturated ketones react with hydrogen peroxide only in a basic medium\(^{37}\) to give epoxide (2) (Scheme 3.1). The function of the base being probably to generate a nucleophilic hydrogen peroxide anion (\(\text{OOH}\)). An 1,4-attack by this species (\(\text{OOH}\)) to form (1) followed by the expulsion of hydroxide ion closes the epoxide ring (2). The epoxide function is cleaved by acid but is stable to base.

![Diagram](image)

**Scheme 3.1**

In order to explore the efficacy of the newly synthesised peroxo-monophosphates, reactions between chalcones and \(\text{Na}_3\text{C}_2\text{PO}_3(\text{O}_2)\cdot3\text{H}_2\text{O}\) (chosen as a representative) were conducted in THF. The reactions
went on quite smoothly to afford the corresponding epoxides (Scheme 3.2) in high yields (vide Experimental)

1. \( R = H \)
2. \( R = OMe \)

**Scheme 3.2**

The Dakin reaction\(^{37}\) is another very characteristic reaction in which hydrogen peroxide in a basic medium is used to convert an aldehydic or a ketonic group ortho to a hydroxylic group to the corresponding dihydroxy compounds. It has been now possible for us to demonstrate that salicylaldehyde readily reacts with the chosen peroxomonophosphate to produce catechol (Scheme 3.3)
Similarly, benzonitrile has been shown to react with 
\( \text{Na}_3 \left[ \text{PO}_3 (\text{O}_2 ) \right] \cdot 7 \cdot 3\text{H}_2 \text{O} \) in an aqueous medium to yield the corresponding amide (Scheme 3.4). This is an interesting reaction, again characteristic of an oxidation otherwise achieved by basic hydrogen peroxide\textsuperscript{37} oxidation.
Further, it is important to note that the new reagent is also capable of bringing about Baeyer-Villiger type of an oxidation. Thus when the substrate benzil was reacted with $\text{Na}_3\left[\text{P}_3\text{O}_3\text{(O}_2\right]_3\text{H}_2\text{O}$ in acetonitrile gave benzoic acid as the end product (Scheme 3.5). A probable mechanism of the reaction is shown in Scheme 3.5.
The results of the reactions described above are very convincing and suggest beyond doubt that sodium peroxomonophosphate trihydrate, \( \text{Na}_3 \left\{ \text{PO}_3 \left(\text{O}_2\right) \right\}_7 \cdot 3\text{H}_2\text{O} \), is a viable substitute for a basic hydrogen peroxide reagent with the additional advantages being that the reagent is a solid one and easy to handle, and maintenance of stoichiometry involving the reagent is also very easy.
This property alone causes us to state that $\text{Na}_3 \overset{\text{PO}_3\text{(O}_2\text{)}}{\text{}} \overset{\text{3H}_2\text{O}}{\text{}}$ is a potential reagent for specific oxidations and in turn is a valuable addition to the wealth of oxidising agents for oxidation of organic substrates.

In our attempt to further explore the properties of sodium peroxomonophosphate, it has been observed that $\text{Na}_3 \overset{\text{PO}_3\text{(O}_2\text{)}}{\text{}} \overset{\text{3H}_2\text{O}}{\text{}}$ is also capable of oxidising alcohols and anthracene. For instance, in stoichiometric reactions with the reagent n-propanol, n-butanol and iso-butanol were oxidised to the corresponding aldehydes (Scheme 3.6) while 2-propanal was found to be oxidized to acetone.

\begin{equation}
\begin{array}{c}
\text{R}-\text{C}-\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} \text{R}-\text{C}-\text{O}\text{H}_2 \xrightarrow{\text{O}-\text{O}-\text{PO}_3} \text{R}-\text{C}-\text{O}-\text{O}-\text{PO}_3 \\
1. \text{R}=\text{C}_2\text{H}_5; \text{R}'=\text{H} \\
2. \text{R}=\text{C}_3\text{H}_7; \text{R}'=\text{H} \\
3. \text{R}=(\text{CH}_3)_2\text{CH}; \text{R}'=\text{H} \\
4. \text{R}=\text{CH}_3; \text{R}'=\text{CH}_3
\end{array}
\end{equation}

Scheme 3.6
The reagent in acetic acid oxidised anthracene to anthraquinone in a high yield (Scheme 3.7)

\[
\begin{array}{c}
\text{Scheme 3.7} \\
\text{Ammonium Peroxo(fluoro)monophosphate Dihydrate,} \\
(NH_4)_2 \left[PO_3(O_2)F\right] \cdot 2H_2O
\end{array}
\]

While investigating some other aspects of phosphorous chemistry (vide Chapter 4), it was observed that a direct interaction of phosphoric acid with alkali hydrogen fluoride, AHF₂, afforded PO₃F²⁻. A similar reaction conducted in the presence of hydrogen peroxide, however, did not give an access to a peroxo-(fluoro)phosphate. Subsequently it was noticed that a raise of pH of the reaction medium and thence isolation of a solid product indicated the formation of a kind of product looked for. Accordingly, the first chemical synthesis of a peroxo(fluoro)phosphate, (NH₄)₂[PO₂(O₂)F] \cdot 2H₂O, was achieved from the reaction of ammonium dihydrogenphosphate with 48% HF and hydrogen peroxide at pH 10-11 maintained by the addition of aqueous ammonia (sp. gr. 0.9)

\[
NH_4H_2PO_4 + HF + H_2O_2 + NH_4OH \rightarrow (NH_4)_2[PO_2(O_2)F] \cdot 2H_2O + 3H_2O
\]
The role of ammonia was not only to raise the pH to facilitate formation of peroxo(fluoro)phosphate but also to act as the source of counter cations, while ethanol helped in precipitating the product. The compound is capable of being stored for a prolonged period in a sealed polyethylene envelope at a freezer temperature, and is insoluble in common organic solvents. It decomposes in water, and thus precludes molar conductance measurement. It liberates H_2O_2 quantitatively in the presence of sulphuric acid rendering it easy to determine the active oxygen content. The results of peroxide estimation and elemental analyses are in complete agreement with the formula (NH_4)_2\(\text{PO}_2\text{O}_2\text{F}_2\)\(\text{H}_2\text{O}\).

The IR spectrum of the compound evidences for the presence of PO, PF and peroxide vibrations. Bands at 1020\text{cm}^{-1} and 1070\text{cm}^{-1} are similar in position to those of the asymmetric stretching of (PO) vibrations, while the absorptions at 950, 550 and 530 \text{cm}^{-1} have been assigned to symmetric (PO) vibrations and \(\delta\) (OPO) modes, respectively. The sharp band at 900 \text{cm}^{-1} is similar in shape and position to that of \(\nu\) (P-F) mode. The band at 855 \text{cm}^{-1} has been assigned to \(\nu\) (O-O) mode of bonded peroxide. The IR spectrum also provides evidence for NH_4^+ and lattice water. The bands at 1400\text{cm}^{-1}, 3040\text{cm}^{-1}, and at 3165\text{cm}^{-1} have been assigned to \(\nu_4\), \(\nu_1\), and \(\nu_3\) modes of NH_4^+. Appearance of \(\nu\) (O-H) at 3400\text{cm}^{-1} and \(\delta\) (H-O-H) at 1660\text{cm}^{-1} conforms well with those one finds for lattice type of water. The laser Raman (1R) spectrum of the solid is in close agreement with its
Table 3.8: Analytical Results and Structurally Significant IR and Raman Bands of Ammonium Peroxo(fluoro)monophosphate Dihydrate, \((\text{NH}_4)_2\text{PO}_2(O_2)^{2-}\text{F}^{+2}\text{H}_2\text{O}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found % (Calcd. %)</th>
<th>IR cm(^{-1})</th>
<th>Raman cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{NH}_4)_2\text{PO}_2(O_2)^{2-}\text{F}^{+2}\text{H}_2\text{O})</td>
<td>14.7 16.8 16.9 9.9</td>
<td>1020s 1070s</td>
<td>1000 1055</td>
<td>(\nu_{as}(\text{PO}))</td>
</tr>
<tr>
<td></td>
<td>(15.06)(16.64)(17.2)(10.21)</td>
<td>950s 530s 550s</td>
<td>950 530 555</td>
<td>(\nu_{s}(\text{PO}))</td>
</tr>
<tr>
<td></td>
<td>900s 855m</td>
<td>900 860</td>
<td>(\delta(\text{P-P}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1660m</td>
<td>860</td>
<td>(\nu(\text{O-O}))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3400s</td>
<td>(\delta(\text{H-O-H}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1400s</td>
<td>(\nu_{4}) (\text{N-H}) modes of (\text{NH}_4^+)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3040s</td>
<td>(\nu_{1})</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3165m</td>
<td>(\nu_{3})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Active Oxygen
$\text{(NH}_4\text{)}_2\text{[PO}_2\text{[O}_2\text{F}]\cdot\text{2H}_2\text{O}}$
i.r. spectrum, and shows signals at 1055 and 1000 cm\(^{-1}\) due to \(\nu_{as}\) (PO) and at 950 cm\(^{-1}\) due to \(\nu_{s}\) (PO). The bands at 555 and 530 cm\(^{-1}\) have been assigned to \(\delta\) (OPO) modes. The peroxo stretching, \(\nu\) (O-O), appears at 860 cm\(^{-1}\). The IR and laser Raman results conform to the formulation of the compound as \((\text{NH}_4)_2 \text{PO}_2\text{O} \cdot \text{F} \cdot 2\text{H}_2\text{O}\) with the peroxide being bonded in an end-on manner as encountered in simple monoperoxo derivatives of sulphur\(^2\) and carbon.\(^1\)

Reactivity of \((\text{NH}_4)_2 \text{PO}_2\text{O} \cdot \text{F} \cdot 2\text{H}_2\text{O}\)

Having achieved the first chemical synthesis of a peroxo-(fluoro)phosphate, \((\text{NH}_4)_2 \text{PO}_2\text{O} \cdot \text{F} \cdot 2\text{H}_2\text{O}\), it was incumbent on us to also study its reactivity. Strategically it was planned to conduct the oxidation reactions under acidic conditions. It is known that hydrogen peroxide in formic acid is capable of hydroxylating alkenes.\(^42\) The reaction is believed to proceed via epoxide formation. We anticipated that the peroxo(fluoro)phosphate might show a similar reactivity. Accordingly, stoichiometric reactions were carried out involving alkenes like 1,2-cyclohexene and styrene in formic acid media with the chosen reagent. The reactions took place smoothly, and the products obtained have been identified to be trans 1,2-cyclohexanediol and 1-phenyl ethyleneglycol (Scheme 3.8). The results of physical studies evidenced that the compounds are exactly similar to those reported in the literature.\(^43,44\) The most probable mechanisms are depicted in Scheme 3.8.
Scheme 3.8
Further, in stoichiometric reactions \((\text{NH}_4)_2\text{PO}_2(O_2)F\cdot 2\text{H}_2\text{O}\) has been found to oxidise n-propanol and n-butanol, in the presence of an acid (dil.\(\text{H}_2\text{SO}_4\)), to the corresponding aldehyde in good yields (Scheme 3.9). Similarly, 2-propanol, a secondary alcohol, has been readily oxidised to acetone by the peroxy-(fluoro)phosphate.

\[
\begin{align*}
\text{R}^\prime & \quad \text{H}_2\text{SO}_4 \\
\text{R} - \text{C} - \text{OH} & \quad \text{R} - \text{C} - \text{OH}_2 \\
& \quad \text{R} - \text{C} - \text{O} - \text{PO}_2\text{F} \\
& \quad \text{HSO}_4^-
\end{align*}
\]

1. \(\text{R} = \text{C}_2\text{H}_5; \text{R}^\prime = \text{H}\)
2. \(\text{R} = \text{C}_3\text{H}_7; \text{R}^\prime = \text{H}\)
3. \(\text{R} = \text{CH}_3; \text{R}^\prime = \text{CH}_3\)

\textbf{Scheme 3.9}

Ammonium peroxy(fluoro)monophosphate was also found to oxidise anthracene to anthraquinone in an acetic acid medium (Scheme 3.10).
Scheme 3.10

The phosphorous product, isolated after working up of the oxidation product in each of the reactions has been identified to be monofluorophosphate, $\text{PO}_3\text{F}^{2-}$, a species important because of its use as an additive in dentifrice formulations. The results obtained so far, on oxidation reactions involving the newly synthesised peroxo(fluoro)phosphate are quite encouraging. It is expected that the compound will be also very useful as an oxidant. Further, studies of reactivity of this reagent, especially under a different set of reaction conditions will be reported elsewhere.

To conclude this Chapter following points may be emphasized. Sodium and ammonium peroxomonophosphate trihydrates, $A_3\sum\text{PO}_3(\text{O}_2)\sum\cdot3\text{H}_2\text{O}$ ($A = \text{Na}$ or $\text{NH}_4$), can be synthesised under suitable experimental conditions. The compounds are white solids and crystalline in nature. Fluorinated peroxophosphate is also capable of being synthesised chemically. First chemical synthesis of such a compound ammonium peroxo(fluoro)phosphate dihydrate, $(\text{NH}_4)_2\sum\text{PO}_2(\text{O}_2)\sum\cdot2\text{H}_2\text{O}$, has been achieved under an appropriate condition. While both types of compounds are highly soluble in
water, but not in common organic solvents, the former ones are comparatively more stable than the latter one.

Both non-fluorinated and fluorinated peroxophosphates have exhibited very interesting oxidation chemistry. Based on the results obtained so far, it is anticipated that these compounds are potential new reagents and they will be significant additions to the wealth of existing oxidising agents.
<table>
<thead>
<tr>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>4. Ref. 2. p. 525.</td>
</tr>
</tbody>
</table>


33. Ref. 31, p. 310.


35. Ref. 31, p. 228.


39. Ref. 34, p. 221.

40. Ref. 31, p. 131.

41. Ref. 34, p. 216.

42. Ref. 29, p. 893.


44. Ref. 43, p. 119.

45. Ref. 6, p. 535.