

## Newer manifestations of reactivity of coordinated peroxide at metal and non-metal centres

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**Abstract.** Newer reactions of coordinated peroxide at metal and non-metal centres are described. Reactions of peroxo-metal complexes with  $\text{SO}_2(g)$ ,  $\text{NO}_2(g)$ , and  $\text{CO}_2(g)$  have been carried out in aqueous medium. Typically, reactions of a highly peroxygenated metal complex,  $\text{A}[\text{V}(\text{O}_2)_3] \cdot 3\text{H}_2\text{O}$  ( $\text{A} = \text{Na}, \text{K}$ ), follow an unprecedented sequence. The deep blue ESR-silent solution of  $\text{A}[\text{V}(\text{O}_2)_3] \cdot 3\text{H}_2\text{O}$  reacts to produce a yellow, ESR-inactive solution that on further reaction with the chosen substrate affords a green-blue ESR-active (cf.  $\text{VO}^{2+}$ ) solution. The reaction proceeds through distinct steps such that, first, one of the coordinated peroxides undergoes a two-electron irreversible cleavage of the O–O bond leading to a diperoxy-mono(sulphato)vanadate(V) intermediate,  $[(\text{O}_2)_2\text{V}-\text{O}-\text{SO}_3]^-$ , that readily undergoes hydrolysis to produce  $\text{H}_2\text{SO}_4$  and an aqua-oxo-diperoxovanadate(V) complex,  $[\text{VO}(\text{O}_2)_2\text{H}_2\text{O}]^-$ . The latter complex reacts with more  $\text{SO}_2(g)$  causing reduction of vanadium (V) to vanadium (IV) and conversion of coordinated peroxide to coordinated sulphate producing the bis(sulphato)vanadyl complex,  $[\text{VO}(\text{SO}_4)_2(\text{H}_2\text{O})_3]^{2-}$ .

Further, the reaction of  $\text{A}[\text{V}(\text{O}_2)_3] \cdot 3\text{H}_2\text{O}$  with  $\text{SO}_2(g)$  in the presence of AF, yielding a ternary fluoro(sulphato)oxovanadate (IV) complex  $\text{A}_4[\text{VO}(\text{SO}_4)_2\text{F}_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ , serves as a paradigm for the synthesis of ternary complexes of vanadyl,  $\text{VO}^{2+}$ . It is also evident *inter alia* that the  $[\text{V}(\text{O}_2)_3]^-$  species offers potential as a novel synthon.

Some recent developments in the peroxo-chemistry of B, C, P and As are highlighted. Heretofore unreported salts of peroxo phosphoric acid, viz.  $(\text{NH}_4)_3[\text{PO}_3(\text{O}_2)] \cdot 3\text{H}_2\text{O}$  and  $\text{Na}_3[\text{PO}_3(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ , have been synthesized and their potential as oxidants explored. Their role in oxidising organic substances is highlighted, especially as a substitute for the alkaline- $\text{H}_2\text{O}_2$  reagent.

**Keywords.** Peroxo-metal and non-metal compounds; reactivity in aqueous media; substitute for the basic- $\text{H}_2\text{O}_2$  reagent.

### 1. Introduction

Information concerning the reactivity of co-ordinated dioxygen is relevant to the understanding of processes involved in the activation of molecular oxygen by metalloenzymes in biological systems as well as in catalytic oxidations (Djordjevic 1982; Mimoun 1983). Peroxides (containing the reduced form of dioxygen) are extremely important reactive intermediates in catalytic oxidations involving molecular oxygen, hydrogen peroxide and alkyl hydroperoxides as the oxygen source (Mimoun 1987). In addition, peroxo complexes are potential oxygen donors to organic and inorganic substrates (Mimoun 1983, 1987) which make them highly useful in industry

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as well as in the laboratory for obtaining a number of valuable oxygenated products such as alcohols, ketones, epoxides, glycols, phenols etc. (Mimoun 1987).

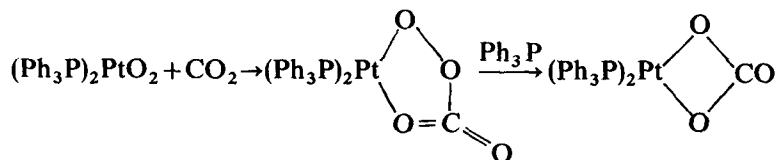
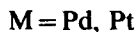
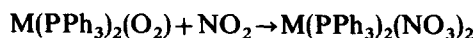
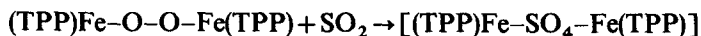
The reactivity of co-ordinated peroxide is dependent on several important criteria such as their solubility, geometry of the compound and availability of vacant co-ordination sites for the binding of the substrate and the overall charge of the reagent.

## 2. Reactivity of metal-peroxo compounds

Peroxo-metal complexes act as 1,3-dipolar reagents  $M^+-O-O^-$  in which the positive charge is localised on the metal and the negative charge on the terminal oxygen atom of the opened peroxo group. They can react with both electrophilic and nucleophilic substrates (Mimoun 1983; Gubelmann and Williams 1983).

Three reactivity zones have been described in case of peroxo-metal complexes which can be distinguished as follows: (i) Mo(VI)- and W(VI) peroxo complexes, which act as heterolytic alkene epoxidation reagents; (ii) V(V)-peroxo and alkylperoxo complexes and Cr(VI) peroxo complexes which act as homolytic hydroxylation reagents; and (iii) Rh(III)-peroxo complexes and alkyl or hydro-peroxo complexes of Rh(III), Ir(III), Pd(II), and Pt(II), which act as heterolytic alkene ketonization reagents (Mimoun 1987).

The reactivity of the co-ordinated dioxygen of low-valent transition metal compounds has received considerable attention in recent years, particularly with respect to its ability to oxidise organic and inorganic substrates, viz. olefins (Takao *et al* 1970; Otsuka *et al* 1972; Dudley *et al* 1974; Tatsuno and Otsuka 1981); carbonyls (Hayward *et al* 1969, 1970; Ugo *et al* 1984); carbon dioxide (Hayward *et al* 1970, 1969), sulphur dioxide (Valentine *et al* 1971; Levison and Robinson 1971; Taqui Khan *et al* 1971; Valentine 1973; Chen-Hwa-Yank *et al* 1974; Miksztal and Valentine 1984; Mehandru and Anderson 1985; Bhattacharjee *et al* 1989a), and nitric oxide (Levison and Robinson 1971). In most of these cases the co-ordinated dioxygen behaves as a nucleophile (Tatsuno and Otsuka 1981). It is evident from the earlier reports that co-ordinated peroxide shows a characteristic reactivity towards inorganic polar substrates like  $SO_2$ ,  $CO_2$ , NO etc. by way of producing co-ordinated sulphate (Valentine *et al* 1971; Valentine 1973), nitrate or carbonate, respectively. Co-ordinated sulphate for example is generated



from the insertion of  $SO_2$  into an  $M-O_2$  bond as evidenced by the isotopic IR study

(Valentine 1973; Tatsuno and Otsuka 1981). Corresponding theoretical studies on the mechanistic details of the steps involved in the formation of  $\text{SO}_4^{2-}$  were also carried out (Mehandru and Anderson 1985). In addition, there have been a number of reports specifically devoted to interaction of  $\text{SO}_2(g)$  with dioxygen-metal complexes (Taqi Khan *et al* 1971; Valentine *et al* 1971; Miksztal and Valentine 1984; Mehandru and Anderson 1985). Despite this progress, there did not exist any information concerning reactions of a highly peroxygenated metal complex with substrates like  $\text{SO}_2(g)$ ,  $\text{NO}_2(g)$ ,  $\text{CO}_2(g)$  etc. until a recent report on the reactivity of a highly peroxygenated vanadium species with  $\text{SO}_2(g)$  (Bhattacharjee *et al* 1989). Moreover, reactions of peroxometallates with such substrates were limited to group VIII metals except that of a peroxotitanium (IV) complex (Miksztal and Valentine 1984). Besides this, most of the earlier results were derived from the studies conducted in non-aqueous medium.

It is evident therefore that an important issue addresses to the pattern of reactivity of a highly peroxygenated metal complex with inorganic substrates like  $\text{SO}_2(g)$ ,  $\text{CO}_2(g)$ ,  $\text{NO}_2(g)$  etc. in an aqueous medium. We considered it worthwhile to select  $\text{SO}_2(g)$ ,  $\text{NO}_2(g)$  and  $\text{CO}_2(g)$  as substrates partly owing to a recognition of the fact that these molecules especially  $\text{SO}_2$  are objectionable atmospheric pollutants (Ryan *et al* 1981) which have detrimental effects on metallo-enzymes in biological systems. Thus the reactivity studies of these molecules with metal-dioxygen complexes are considered to be useful to get an insight into the details of mechanism as well as the course of such reactions.

It was imperative then to investigate such reactions and to rationalise the reaction sequence by isolating products at different stages. Recently, it has been discovered that a minimum of three  $\text{O}_2^-$  per vanadium (V) centre are required for the formation of a blue colour of the V-H<sub>2</sub>O<sub>2</sub> system (Chaudhuri and Islam 1985b) owing to the formation of the complex  $[\text{V}(\text{O}_2)_3]^-$  species. The interest in reactivity of co-ordinated peroxide at a vanadium(V) centre stems from its occurrence as an essential trace element in biological systems (Mertz 1981; Ramasarma and Crane 1981; Chasteen 1983; Tracey and Graser 1986). Recent information concerning participation of vanadium in stimulating nitrogen fixation (Robson *et al* 1986), its role as an intermediate electron carrier in the oxidation of NADH (Rau *et al* 1987), as a biological hydrogen abstractive agent and active involvement of the V-H<sub>2</sub>O<sub>2</sub> system in some biochemical processes (Djordjevic and Wampler 1985; Patole *et al* 1987), and the capacity of peroxyvanadium complexes to oxidize organic substrates (Mimoun *et al* 1986; Chaudhuri 1988) are very exciting contributions to the current knowledge of biochemical and catalytic involvement of the metal.

Thus, because of the rich diversity and practical utility of peroxyvanadate(V) system (Clark and Brown 1975; Chaudhuri and Ghosh 1982, 1984; Djordjevic 1982; Campbell *et al* 1983; Schwendt and Joniakova 1984; Chaudhuri and Islam 1985; Djordjevic and Wampler 1985; Mimoun *et al* 1986; Stomberg 1986; Chaudhuri 1988), the  $[\text{V}(\text{O}_2)_3]^-$  species was considered a suitable candidate for the proposed reactivity studies. An additional object was to ascertain whether the co-ordinated peroxide or the metal centre reacted with inorganic substrates like  $\text{SO}_2(g)$  in preference, when both are capable of participating in electron-transfer reactions with the chosen substrates. We have investigated reactions of the species with three substrates, viz.  $\text{SO}_2(g)$ ,  $\text{CO}_2(g)$  and  $\text{NO}_2(g)$ .

### 3. Reactions of $A[V(O_2)_3] \cdot 3H_2O$ ( $A = Na, K$ ) with $SO_2(g)$ , $NO_2(g)$ or $CO_2(g)$ in aqueous media

The reaction of  $A[V(O_2)_3] \cdot 3H_2O$  with  $SO_2(g)$  is detailed as a representative case. Quite a different kind of reactivity pattern has been observed in the reaction of  $SO_2(g)$  with a highly peroxygenated vanadium(V) centre. The reactions were studied by following the reaction sequence through the isolation of compounds at various stages of the reactions. It was also our concern to explore the possibility of obtaining mixed-ligand peroxy sulphato vanadate (V) compounds that were inaccessible so far (Chaudhuri and Islam 1985). We expected that this would be possible by the interaction of one of the co-ordinated  $O_2^-$  ligands through an insertion of  $SO_2$  into the O–O bond in a manner similar to that with the mono-peroxo complex (Valentine 1973; Miksztal and Valentine 1984). Strategically the reactions were conducted in aqueous media because studies made by previous workers were carried out in non-aqueous media. This was possible as the triperoxo vanadate (V) compounds are soluble and stable in water at least under our experimental conditions.

The deep blue  $A[V(O_2)_3] \cdot 3H_2O$  in solution readily reacted with  $SO_2(g)$ , as evident from the colour change from deep blue to yellow and finally to green-blue. In separate experiments, the flow of  $SO_2(g)$  was discontinued at each stage of the colour change, followed by attempts to isolate the compounds. The pH values of the yellow and green-blue solutions have been determined to be  $\approx 6$  and  $\approx 2$ , respectively. From the intermediate yellow solution a yellow solid precipitated spontaneously only in the case of the potassium salt. This was highly soluble and stable in water. The results of chemical analyses give the stoichiometry of  $K:V:O_2^-$  as 1:1:2 and the molar conductance in water as  $135 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ , clearly indicating the 1:1 electrolytic nature of the product. On the basis of this information and the results of other physical studies, the yellow intermediate has been characterised as potassium aquaoxidiperoxovanadate(V)  $K[VO(O_2)_2(H_2O)]$ .

It is quite significant that the intermediate yellow solution and also the aqueous solution of the yellow compound made after it was isolated did not show any ESR signals, suggesting beyond doubt that the metal did not undergo any reduction so far. It may be mentioned that the solid  $K[V(O_2)_3] \cdot 3H_2O$  and its deep blue aqueous solution were ESR-silent, as expected for a triperoxovanadate(V) species. The significant features of the IR spectrum of the yellow compound involve bands due to co-ordinated peroxide and water and  $V=O$  stretching. Interestingly, no characteristic band for sulphate was observed, and its absence was also ascertained independently by chemical analysis. This is an unusual kind of observation because all other studies reported until date led to the insertion of  $SO_2$  into the O–O bond of  $O_2^-$  leading to co-ordinated  $SO_4^{2-}$  (Tatsuno and Otsuka 1981; Miksztal and Valentine 1984). In the present case, however, instead of S–O modes, a strong band appears at  $950 \text{cm}^{-1}$  which has been assigned to  $\nu(V=O)$ . The peroxo modes as observed in the IR and LR spectra are characteristic of a chelated  $(C_{2v})O_2^-$  group (Chaudhuri and Ghosh 1982, 1984).

The origin of the oxo-oxygen of the yellow intermediates is believed to be one of the co-ordinated  $O_2^-$  groups. Presumably,  $SO_2$  insertion took place in the O–O bond of the peroxide group to form a sulphatodiperoxovanadate(V) species,  $[V(SO_4)(O_2)_2]^-$ , which readily underwent hydrolysis to produce the yellow aquaoxidiperoxovanadate(V) complex,  $[VO(O_2)_2(H_2O)]^-$ , as isolated, and  $H_2SO_4$ .

The formation of an oxo species over that of a sulphato is unusual but certainly not unprecedented. It was observed a few years ago that the  $\text{TiOEP}(\text{O}_2)$  with  $\text{SO}_2$  underwent ready hydrolysis even in the presence of moisture giving  $\text{Ti}(\text{O})\text{OEP}$  and  $\text{H}_2\text{SO}_4$  (Nakajima *et al* 1977). It is pertinent to mention here that results of an earlier investigation showed, co-ordination of  $\text{SO}_4^{2-}$  to V(V) in presence of peroxide to be a difficult task (Chaudhuri and Islam 1985), although definitive reasons for this could not be discerned at the moment.

The reaction of  $\text{A}[\text{V}(\text{O}_2)_3] \cdot 3\text{H}_2\text{O}$  with  $\text{SO}_2(\text{g})$ , without being arrested at a stage of yellow colouration, ultimately generated a green-blue solution ( $\text{pH} \approx 2$ ) that did not undergo any further colour change under our experimental conditions. The ESR spectrum of this solution exhibited a pattern typical of an oxo-vanadium (IV) species. The blue compound isolated from the solution was different from the yellow one in terms of colour as well as its physical properties, viz. the magnetic moment, oxidation states of the metal, and the kinds of ligands present. The blue compound was finally characterized as a triaquabis(sulphato)oxo-vanadate(IV) complex,  $\text{A}_2[\text{VO}(\text{SO}_4)_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$  ( $\text{A} = \text{Na}, \text{K}$ ).

The ESR spectra of aqueous solutions of the compounds recorded both at ambient temperatures and at 77 K showed signals at  $g_{\text{av}} = 1.992$ , typical of an oxovanadium (IV) species, suggesting that the complexes exist as monomers. The IR and LR spectra of the compounds showed the complete absence of peroxide, which was further ascertained by chemical analysis. The spectra clearly indicated the occurrence of co-ordinated sulphate bonded to the V(IV) centre in a unidentate ( $\text{C}_{3v}$ ) manner. Although the reaction of  $\text{SO}_2$  with chelated  $\text{O}_2^{2-}$  invariably gave rise to a chelated  $\text{SO}_4^{2-}$  (Valentine 1973; Tatsuno and Otsuka 1981) the present observation is apparently peculiar. However, this mode of co-ordination seems to be rather typical of sulphato complexes of vanadium (IV) (Balhausen *et al* 1968).

From a perusal of the course of the reactions described above, it was anticipated that similar reactions in the presence of a suitable ligand might afford ternary complexes of vanadium (IV). It has been known that vanadyl,  $\text{VO}^{2+}$ , binds the most electronegative atoms very effectively, of which the fluoro complexes are especially stable (Clark and Brown 1975). Accordingly, the reactions of  $\text{A}[\text{V}(\text{O}_2)_3] \cdot 3\text{H}_2\text{O}$  with  $\text{SO}_2(\text{g})$  were conducted in the presence of alkali-metal fluoride. Here again, the spectrum of colour changes was similar to that observed earlier, ultimately producing a green-blue ESR-active (cf.  $\text{VO}^{2+}$ ) solution. Working-up of the solution afforded a blue solid containing both fluoride and sulphate as anticipated. On the basis of the results of various physico-chemical studies, the compounds have been formulated as  $\text{A}_4[\text{VO}(\text{SO}_4)_2\text{F}_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  ( $\text{A} = \text{Na}, \text{K}$ ). The  $\text{SO}_4^{2-}$  binds the  $\text{VO}^{2+}$  centre in a unidentate manner and the complex  $[\text{VO}(\text{SO}_4)_2\text{F}_2(\text{H}_2\text{O})]^{4-}$  species occurs as a hexacoordinated monomer. Thus it is evident that the  $[\text{V}(\text{O}_2)_3]^-$  species offers potential as a novel synthon.

The results of the above investigation prompted us to extend such reactivity studies to different inorganic substrates and also to other metal-dioxygen systems in aqueous media so that some important generalisations could be drawn.

Interestingly, interaction of  $\text{NO}_2(\text{g})$  or  $\text{CO}_2(\text{g})$  with the  $[\text{V}(\text{O}_2)_3]^-$  species in aqueous media resulted in a spectrum of colour changes of the reaction solution from yellow to green-blue, similar to that observed in case of its reaction with  $\text{SO}_2(\text{g})$ . However, the reactions with  $\text{NO}_2(\text{g})$  or  $\text{CO}_2(\text{g})$  were relatively slower. In these cases also, a yellow solid precipitated spontaneously from the yellow solution. Incidentally, the

yellow intermediate was ascertained to be  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$ , similar to that obtained in the case of the corresponding  $\text{SO}_2(g)$  reaction. It is pertinent to mention here that during the reactivity study of the  $[\text{V}(\text{O}_2)_3]^-$  species with  $\text{SO}_2(g)$ , although the yellow colour was observed in both  $\text{Na}^+$  and  $\text{K}^+$  salts, the yellow intermediate could, however, be isolated in the solid state only as its potassium salt, viz.  $\text{K}[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]$ , whereas reaction with  $\text{NO}_2(g)$  or  $\text{CO}_2(g)$  afforded the isolation of the  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$  species both as  $\text{Na}^+$  and  $\text{K}^+$  salts.

The reaction of  $\text{A}[\text{V}(\text{O}_2)_3] \cdot 3\text{H}_2\text{O}$  with  $\text{NO}_2$  or  $\text{CO}_2$  ultimately generated a deep green-blue solution ( $\text{pH} \approx 2$ ) that did not undergo any further colour change on prolonged bubbling of the reactant gases. The green-blue solution which also afforded a green product showed the presence of vanadium (IV) and  $\text{NO}_3^-$  or  $\text{CO}_3^{2-}$  in the respective cases and a complete absence of  $\text{O}_2^{2-}$ .

Taking note of the yellow and green solutions and the products obtained therefrom, it can be seen that here also it is one of the peroxo groups which reacts with  $\text{NO}_2$  or  $\text{CO}_2$  preferentially over the V(V) centre giving rise to the oxo-diperoxo species of vanadium(V),  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$ . Ultimately the vanadium (V) centre gets reduced by the substrates,  $\text{NO}_2$  or  $\text{CO}_2$ , although the second step is rather slow as expected.

Following are the important points that emerge from our reactivity studies on peroxo-vanadium systems with the three substrates, viz.  $\text{SO}_2(g)$ ,  $\text{NO}_2(g)$  and  $\text{CO}_2(g)$  in aqueous medium:

(i) The interaction of highly peroxygenated vanadium(V) species,  $[\text{V}(\text{O}_2)_3]^-$ , with  $\text{SO}_2(g)$ ,  $\text{NO}_2(g)$  and  $\text{CO}_2(g)$  in aqueous media follow a novel reaction sequence. While both co-ordinated peroxide and the metal centre are prone to undergo electron-transfer reactions with the chosen inorganic substrates, the present experiments clearly demonstrate that it is one of the edge-bound peroxide ligands that participates in the reaction in preference to vanadium (V).

(ii) The reaction proceeds through distinct steps. For example, when  $\text{SO}_2$  reacts with  $[\text{V}(\text{O}_2)_3]^-$ , first, one of the co-ordinated peroxides undergoes a two-electron irreversible cleavage of the O–O bond leading to a diperoxo-mono(sulphato)vanadate (V) intermediate,  $[(\text{O}_2)_2\text{-V-O-SO}_3]^-$ , that readily undergoes hydrolysis to produce  $\text{H}_2\text{SO}_4$  and the aquaoxidiperoxovanadate(V) complex,  $[\text{VO}(\text{O}_2)(\text{H}_2\text{O})]^-$ , isolated in the solid state as its salt. Similar processes are also involved in the reaction of  $[\text{V}(\text{O}_2)_3]^-$  with  $\text{NO}_2(g)$  or  $\text{CO}_2(g)$  producing similar intermediate peroxo species and the corresponding acids.

(iii) The reaction of  $[\text{V}(\text{O}_2)_3]^-$  with the aforesaid substrates in aqueous media provide a general and easily accessible route to the synthesis of a novel complex  $[\text{VO}(\text{O}_2)_2 \cdot (\text{H}_2\text{O})]^-$  species, as an isolable intermediate. This species is expected to be a potential synthetic precursor for the synthesis of heteroligand diperoxo complexes of vanadium(V) since it contains a labile ligand,  $\text{H}_2\text{O}$ , which can be replaced by other suitable ligands of interest (L) to gain access to a host of complexes of the type  $[\text{VO}(\text{O}_2)_2\text{L}]^-$ .

(iv) The complex  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$  reacts with further amounts of  $\text{SO}_2(g)$  causing reduction of V(V) to V(IV) and conversion of co-ordinated sulphate producing bis(sulphato) vanadyl complex  $[\text{VO}(\text{SO}_4)_2(\text{H}_2\text{O})_3]^{2-}$  which can be isolated in the solid state.

(v) Further reaction of  $[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]^-$  with  $\text{CO}_2$  or  $\text{NO}_2$  leads to the ultimate formation of a product in which vanadium centre is reduced to the +4 state. The  $\text{NO}_3^-$  and  $\text{CO}_3^{2-}$  formed by the interaction of  $\text{O}_2^{2-}$  pass on to the solution instead

of co-ordinating to the metal centre. The ultimate reaction product isolated in the solid state in these two reactions is an oxovanadium species.

(vi) The reaction of  $[\text{V}(\text{O}_2)_3]^-$  species with  $\text{SO}_2(g)$  in the presence of alkalifluoride in aqueous medium leading to a ternary complex of vanadium(IV), viz.  $[\text{VO}(\text{SO}_4)_2\text{F}_2(\text{H}_2\text{O})]^{4-}$ , qualifies the  $[\text{V}(\text{O}_2)_3]^-$  species as a potential synthon.

#### 4. Reactions of $\text{A}_3[\text{Ti}(\text{O}_2)\text{F}_5]$ ( $\text{A} = \text{NH}_4, \text{K}$ or $\text{Na}$ ) with $\text{SO}_2(g)$ or $\text{NO}_2(g)$ and $\text{NH}_4[\text{ZrO}(\text{O}_2)\text{F}_2]$ with $\text{SO}_2(g)$ in aqueous media

As proposed earlier in this paper, in order to obtain an insight into the reactivity of peroxo-metallates with the chosen substrates in aqueous media, reactions involving other metal peroxo compounds have also been studied.

In an earlier communication we have described the synthesis of  $\text{A}_3[\text{Ti}(\text{O}_2)\text{F}_5]$  ( $\text{A} = \text{NH}_4, \text{Na}$  or  $\text{K}$ ) (Chaudhuri and Das 1986). The yellow-coloured monoperoxo-fluoro complexes of Ti(IV) are soluble and stable in aqueous solution at ambient temperatures which enabled us to carry out the reactivity studies in aqueous medium. The yellow complex  $[\text{Ti}(\text{O}_2)\text{F}_5]^{3-}$  reacted rapidly with the substrates  $\text{SO}_2(g)$  or  $\text{NO}_2(g)$  ultimately giving rise to a clear colourless solution (pH 2). Unlike in the case of highly peroxygenated vanadium(V) complexes, we did not expect any isolable intermediate in this case because of the presence of only one peroxo group in its co-ordination sphere.

Working up of the colourless solution afforded a white microcrystalline product in each of the reactions. The complex species did not contain any co-ordinated  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  as confirmed from various physico-chemical studies. The IR and LR spectra of the white microcrystalline reaction product proved the complete absence of co-ordinated peroxide and showed the presence of co-ordinated fluoride and lattice water. The titanium centre remained unreduced in the reaction product as expected. On the basis of studies as mentioned above, the ultimate white reaction product has been formulated as  $\text{A}_2[\text{TiF}_6]$ .

The mother liquor obtained after isolating the white product of the reaction between  $\text{A}_3[\text{Ti}(\text{O}_2)\text{F}_5]$  with  $\text{SO}_2(g)$  or  $\text{NO}_2(g)$ , showed the occurrence of  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$ , respectively. This implied that the electron-transfer reaction between bonded  $\text{O}_2^{2-}$  and  $\text{SO}_2$  or  $\text{NO}_2$  did take place as anticipated, however, the corresponding  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  did not remain co-ordinated to the metal centre, instead they passed on to the solution. This may be explained in terms of the high thermodynamic stability of the  $[\text{TiF}_6]^{2-}$  species as evident from a perusal of the familiar chemistry of Ti(IV). Therefore, the formation of hexafluorotitanate(IV) species was favoured over the corresponding fluoro-sulphato or fluoro-nitrato titanate(IV).

The reactivity of another peroxo-metal system, viz.  $(\text{NH}_4)_2[\text{ZrO}(\text{O}_2)\text{F}_2]$ , with  $\text{SO}_2(g)$  in an aqueous medium has also been investigated. The complexes  $\text{A}_2[\text{ZrO}(\text{O}_2)\text{F}_2]$  ( $\text{A} = \text{Na}, \text{K}, \text{NH}_4$ ) have been synthesised for the first time in this laboratory (Bhattacharjee *et al* 1990a), which made it readily accessible for the purpose of reactivity studies. In a representative reaction, the complex  $(\text{NH}_4)_2[\text{ZrO}(\text{O}_2)\text{F}_2]$  was allowed to react with  $\text{SO}_2(g)$  in aqueous medium. This led to the isolation of a white product that has been shown to contain  $\text{SO}_4^{2-}$  and  $\text{F}^-$  bonded to the Zr(IV) centre. Based on the results of various studies, the white complex has been formulated as  $(\text{NH}_4)_2[\text{ZrO}(\text{SO}_4)\text{F}_2] \cdot 7\text{H}_2\text{O}$ . The  $\text{SO}_4^{2-}$  binds the Zr(IV) centre in a chelated fashion, unlike the case of the peroxo-titanate(IV) reaction described above.

Studies involving similar substrates with peroxo-metal systems having different metal centres with various stoichiometries are now underway in this laboratory in our endeavour to demonstrate some newer facets of the reaction chemistry of peroxo-metal complexes.

## 5. Reactivity of non-metal peroxo compounds

As opposed to a number of reports on the reactions of peroxo-metal compounds, non-metal peroxo compounds have not received due attention, and thus comparatively very little is known in the literature about non-metal peroxo species (DeMarco and Shreeve 1974). A few peroxo-compounds of non-metals like carbon (Jones and Griffith 1980), sulphur (Simon and Richter 1957; Cotton and Wilkinson 1988), phosphorus (Toy 1975) etc. are known and some of them were shown to have practical applications (Boyland *et al* 1953; Kennedy and Stock 1960; Dhar and Munjal 1973; Ogata *et al* 1974, 1978, 1979). However, synthetic routes to many of these compounds are not straightforward and, further, studies of the reactivities of such compounds are rather limited. In our studies (Chaudhuri 1988) on the synthesis, characterisation, structural assessment and reactivity of peroxocompounds, we also included non-metals.

Boron is known to form compounds with hydrogen peroxide. For example, peroxoborates of the type  $\text{Na}_2[\text{B}_2(\text{O}_2)(\text{OH})_4]$  (Hanson 1961; Greenwood 1975) is known in the literature and is used widely as an oxidising component in many detergent formulations. While, simple peroxoborates were known in the literature, no hetero-peroxo compounds of boron were known until recently (Chaudhuri and Das 1985), when it was shown that peroxofluoroborates of the types  $\text{A}_2[\text{B}(\text{O}_2)\text{F}_3] \cdot 4\text{H}_2\text{O}$  ( $\text{A} = \text{Na}$  or  $\text{K}$ ), (1), and  $(\text{NH}_4)_2[\text{B}_2(\text{O}_2)_3\text{F}_2]$ , (2), were capable of being synthesised. In view of the oxidising capability of simple peroxoborate, it is anticipated that the newly synthesised compounds will be potential oxidising agents and work in this direction has already been initiated.

Similar to the boron complexes, simple peroxocarbonates  $\text{A}[\text{HCO}_4]$  ( $\text{A} = \text{K}$  or  $\text{Na}$ ) are known (Jones and Griffith 1980) and are prepared from a reaction of  $\text{CO}_2(\text{g})$  with 50–86%  $\text{H}_2\text{O}_2$  in basic medium. However, this route to  $\text{AHCO}_4$  does not appear to be a convenient one, for it needs a very highly concentrated solution of  $\text{H}_2\text{O}_2$  and also an extra preparative step of hydroperoxide as the precursor. Thus it was thought worthwhile to develop a simple route to heretofore unreported  $(\text{NH}_4)[\text{HCO}_4] \cdot 3\text{H}_2\text{O}$  (3) and then study its reactivity.

The synthesis was achieved (Bhattacharjee *et al* 1990b) from a reaction of 30%  $\text{H}_2\text{O}_2$  with ammoniacal solution of  $\text{NH}_4\text{HCO}_4$  at pH 9.5 at 0 to  $-2^\circ\text{C}$ . The new method has advantages as it does not involve a highly concentrated solution of  $\text{H}_2\text{O}_2$ , the extra preparation of hydroperoxide or the redundancy of use of  $\text{CO}_2(\text{g})$ .

Similarly phosphorus peroxo compounds have been dealt with in the literature, however, they have received very scant attention. For example, the importance of peroxomonophosphoric acid has been highlighted in the literature (Toenies 1937; Lake and Mamantov 1963) but it is not very easy to obtain. Further, free peroxomonophosphoric acid does not permit easy isolation (Lethbridge and Heslop 1964).

Despite the difficulties in obtaining peroxomono-phosphoric acid, it has generated some interest especially because of its versatile oxidising properties. Thus it was



imperative to synthesise the salts of the acid and explore their properties particularly in terms of their reactivities.

Apart from the above, hetero-peroxo compounds of non-metal in general, and of phosphorus in particular, are very poorly investigated. It was reported over half a century ago (Garcia 1933) 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  $\approx 2\%$  yields. The compounds were poorly characterised and to our knowledge neither salts of the acid nor any chemical synthesis of fluorinated peroxophosphate were reported until the first chemical synthesis was published by us recently (Bhattacharjee and Chaudhuri 1988).

The syntheses (Bhattacharjee and Chaudhuri 1989b) of ammonium and sodium peroxomonophosphate,  $(\text{NH}_4)_3[\text{PO}_3(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ , (4), and  $\text{Na}_3[\text{PO}_3(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ , (5), were achieved from reactions of  $\text{A}_2\text{HPO}_4$  ( $\text{A} = \text{NH}_4, \text{Na}$ ) with 30%  $\text{H}_2\text{O}_2$  at pH 9.5. Likewise, the first chemical synthesis of a fluorinated peroxophosphate  $(\text{NH}_4)_2[\text{PO}_2(\text{O}_2)\text{F}] \cdot 2\text{H}_2\text{O}$ , (6), was achieved from a reaction of  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  with 48% HF and hydrogen peroxide at pH 10–11.

The compounds are white crystalline solids insoluble in common organic solvents, but highly soluble in water in which they decompose.

Having achieved the syntheses of simple peroxo and fluoro-peroxo compounds of phosphorus, we were interested in synthesising the analogous compounds of arsenic. To our knowledge no definite peroxo compound of arsenic is reported to date, although  $\text{As}_2\text{O}_3$  is used as a catalyst for oxidation of organic substrates by  $\text{H}_2\text{O}_2$  (McMullen 1977). Accordingly two reactions were carried out between  $\text{As}_2\text{O}_3$  and 30%  $\text{H}_2\text{O}_2$  at pH 9.6 and between  $\text{As}_2\text{O}_3$  and  $\text{H}_2\text{O}_2$  in the presence of  $\text{NH}_4\text{F}$  and 48% HF at pH 9. While the former reaction afforded a hydroperoxo species,  $(\text{NH}_4)_2[\text{AsO}_3(\text{OOH})] \cdot \text{H}_2\text{O}$ , (7), the latter reaction provided a peroxo-fluoro arsenate(V),  $(\text{NH}_4)_2[\text{As}_2\text{O}_4\text{F}_2(\text{O}_2)] \cdot 6\text{H}_2\text{O}$ , (8) (Bhattacharjee *et al* 1990b).

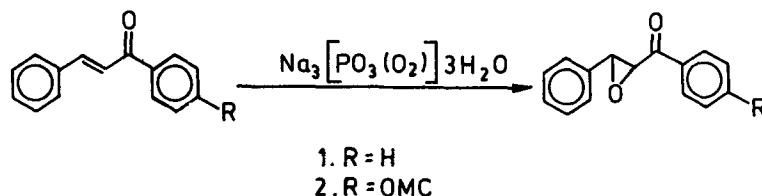
All these compounds were characterised by elemental analyses, IR and laser Raman spectroscopic studies and molar conductance measurements. In all the peroxo-compounds synthesised except in those of boron, the peroxide is bonded in an end-on manner and in  $(\text{NH}_4)[\text{AsO}_3(\text{OOH})] \cdot \text{H}_2\text{O}$ , (7), peroxide occurs as a hydroperoxide. In peroxofluoroborates, peroxide is found to be bonded in a  $\text{C}_{2v}$  fashion. A measurement of the pH of 0.01M solutions of the peroxo compounds of carbon,  $(\text{NH}_4)[\text{HCO}_4] \cdot 3\text{H}_2\text{O}$ , (3), phosphorus,  $(\text{NH}_4)_3[\text{PO}_3(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ , (4),  $\text{Na}_3[\text{PO}_3(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ , (5), and  $(\text{NH}_4)_2[\text{PO}_2(\text{O}_2)\text{F}] \cdot 2\text{H}_2\text{O}$ , (6), and those of arsenic,  $(\text{NH}_4)_2[\text{AsO}_3(\text{OOH})] \cdot \text{H}_2\text{O}$ , (7) and  $(\text{NH}_4)_2[\text{AsO}_4\text{F}_2(\text{O}_2)] \cdot 6\text{H}_2\text{O}$ , (8) showed that the solutions are basic in nature. The pH values were 8.5, 7.9, 8.9, 7.9, 9, and 8.5, respectively.

Having achieved the syntheses of these compounds, we sought to study their reactivities, particularly in terms of the reactivity of the bonded peroxide. It may be recalled here that the aqueous solutions of the newly synthesised compounds of C, P, and As are basic in nature and this particular observation led us to anticipate that these compounds might show a type of reactivity different from those of metal-peroxo compounds. Due to the presence of peroxide and the basic nature of these compounds they are expected to be capable of being used as viable substitutes for the basic- $\text{H}_2\text{O}_2$  reagent with some added advantages, viz. ease of handling and maintenance of required stoichiometry.

Typically  $\alpha$ ,  $\beta$ -unsaturated ketones react with hydrogen peroxide only in basic

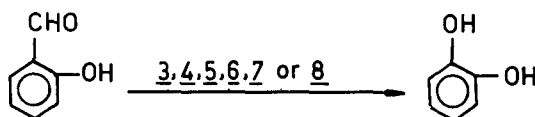
media (Fieser and Fieser 1967) to give epoxides. The function of the base is probably the generation of a nucleophilic hydrogen peroxide anion(OOH), which then forms epoxide by 1,4 attack.

In order to explore the efficacy of the newly synthesised compounds, reactions between chalcones in THF solutions and aqueous solutions of the peroxy compounds 3, 4, 5, 6, 7, and 8, were separately carried out. However, in only the case of  $\text{Na}_3[\text{PO}_3(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ , (5), did the reactions go quite smoothly to afford the corresponding epoxides in high yields (scheme 1). In the case of the other compounds



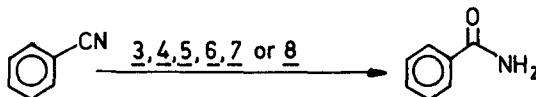
Scheme 1

no epoxide formation could be observed. The reason for this may be that the compound  $\text{Na}_3[\text{PO}_3(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ , (5), provides the optimum pH for this conversion. The Dakin reaction (Fieser and Fieser 1967) is another very characteristic reaction in which hydrogen peroxide in basic medium is used to convert an aldehydic or ketonic group ortho to a hydroxylic group to the corresponding dihydroxy compounds. It has now been possible for us to demonstrate that salicylaldehyde readily reacts with an aqueous solution of 3, 4, 5, 6, 7, or 8 to produce catechol (scheme 2).



Scheme 2

Similarly, an ethanolic solution of benzonitrile has been shown to react with 3, 4, 5, 6, 7, or 8 at  $\approx 50^\circ\text{C}$  to yield the corresponding amide (scheme 3). This is an



Scheme 3

interesting reaction, again characteristic of oxidation otherwise achieved by the basic peroxide reagent (Fieser and Fieser 1967).

Further, it is important to note that the compounds 4, 5, 6, 7, and 8 are also capable of bringing about Baeyer–Villiger type of oxidation (Panda *et al* 1988). Thus when benzil in acetonitrile medium is reacted with an aqueous solution of the compounds 4, 5, 6, 7, or 8 benzoic acid is the end product.

The results of the reactions described above are very convincing and suggest beyond doubt that these compounds are viable substitutes for the basic hydrogen peroxide reagent, with the additional advantages that the reagents are solid and easy to handle, and that maintenance of stoichiometry involving the reagents is also very easy. This property alone leads us to state that the peroxy compounds of C, P and As described

herein are potential reagents for specific oxidations and in turn are valuable additions to the number of oxidising agents for use with organic substrates.

In our attempts to further explore the properties of these compounds, a few more reactions involving  $\text{Na}_3[\text{PO}_3(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ , (5), and  $(\text{NH}_4)_2[\text{PO}_2(\text{O}_2)\text{F}] \cdot 2\text{H}_2\text{O}$ , (6), were carried out in acid media. For example  $\text{Na}_3[\text{PO}_3(\text{O}_2)] \cdot 3\text{H}_2\text{O}$ , (5), or  $(\text{NH}_4)_2[\text{PO}_2(\text{O}_2)\text{F}] \cdot 2\text{H}_2\text{O}$  when reacted with alcohols such as *n*-propanol, *n*-butanol, iso-butanol or 2-propanol in aqueous media in the presence of a few drops of conc.  $\text{H}_2\text{SO}_4$ , oxidised them to the corresponding carbonyl compounds (aldehydes and ketone). Anthracene when reacted with these compounds in acetic acid medium afforded anthraquinone.

In another set of reactions involving  $(\text{NH}_4)_2[\text{PO}_2(\text{O}_2)\text{F}] \cdot 2\text{H}_2\text{O}$ , (6), in formic acid medium, cyclohexene and styrene were oxidised to 1,2-cyclohexanediol and 1-phenyl-1, 2-ethanediol, reactively, at ambient temperature. The results obtained so far from the study of the reactivity of these compounds lead us to emphasise that non-metal peroxy compounds are no less potential reagents than metal-peroxy compounds.

## 6. Conclusion

In conclusion it may be mentioned that research on the chemistry of the peroxy compounds of metals as well as non-metals offers wide scope and appears to be very rewarding especially in the context of biomimetic modelling and catalytic oxidations of a variety of substrates. Although considerable progress has been made in this field, it continues to be an active area of contemporary inorganic research. There is every indication that the studies on the reactivities of metal and non-metal peroxy compounds in aqueous media with various organic substrates and small inorganic molecules will generate newer information. More attention also needs to be paid to studies involving non-metal peroxy species including their reactivities.

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