

Synthesis and structural characterization of peroxoarsenates, $(\text{NH}_4)_2[\text{AsO}_3(\text{OOH})]\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)_2[\text{As}_2\text{O}_4(\text{O}_2)\text{F}_2]\cdot 6\text{H}_2\text{O}$

Mihir K Chaudhuri*, Gagan C Mandal & Pradip C Paul

Department of Chemistry, North-Eastern Hill University,
Shillong 793 003, India

Received 4 July 1996; revised 22 August 1996

The peroxoarsenates(V), of the formulae $(\text{NH}_4)_2[\text{AsO}_3(\text{OOH})]\cdot\text{H}_2\text{O}$ (**1**) and $(\text{NH}_4)_2[\text{As}_2\text{O}_4(\text{O}_2)\text{F}_2]\cdot 6\text{H}_2\text{O}$ (**2**) have been synthesised and characterized by elemental analysis, solution electrical conductance measurement, gas-volumetric analyses in respect of the active oxygen contents, IR and laser Raman spectroscopic studies. Typically, **1** and **2** transform salicylaldehyde to catechol, benzonitrile to benzamide, and benzil to benzoic acid in good yields. Sulphur dioxide is readily converted to sulphate in aqueous medium. Independent evidence for the oxidation of arsenic(III) to arsenic(V) has also been provided.

The area of non-transition metal peroxo chemistry, as opposed to that of transition metals, has received a rather scant attention. As a case in point, for instance, very little is known about peroxo compounds of arsenic¹ despite an extensive use of its oxides such as As_2O_3 , AsO_4^{3-} , in the presence of H_2O_2 for the selective as well as catalytic oxidations of a variety of organic substrates². While studying the peroxo chemistry of some other metals³, our attention was drawn to this aspect of arsenic and we sought to synthesise such compounds. Strategically, the formation of peroxoarsenate would also require the oxidation of arsenic(III) to arsenic(V). Therefore, the synthetic reactions were planned in aqueous alkaline media in the presence of an excess of H_2O_2 .

The present paper reports the synthesis of peroxoarsenic(V) compounds of the types $(\text{NH}_4)_2[\text{AsO}_3(\text{OOH})]\cdot\text{H}_2\text{O}$ (**1**) and $(\text{NH}_4)_2[\text{As}_2\text{O}_4(\text{O}_2)\text{F}_2]\cdot 6\text{H}_2\text{O}$ (**2**), their structural characterization and highlights the results of a few reactions with some organic substrates as well as sulphur dioxide.

Experimental

All the chemicals were of reagent grade and used without further purification. IR and laser Raman (LR) spectra were recorded by the meth-

ods reported elsewhere³. A systronics Type 335 digital pH-meter and pH indicator (BDH) paper were used to measure the pH values. Solution electrical conductance was measured using a Wayne Kerr Automatic Precision Bridge B 905 conductometer. The synthesis of **2** was carried out in a polyethylene apparatus.

The reactions of **1** and **2** were carried out under pure N_2 atmosphere using deaerated water⁴.

Synthesis

Ammonium hydrogenperoxotrioxoarsenate(V) monohydrate $(\text{NH}_4)_2[\text{AsO}_3(\text{OOH})]\cdot\text{H}_2\text{O}$ (**1**)

To arsenic trioxide (1 g, 5.1 mmol) in a 100 ml beaker was added 15 ml of 30% (H_2O_2 , 132.35 mmol) while stirring for ~ 10 min. The pH of the reaction solution was then raised slowly with constant stirring to 9.5 by the addition of aqueous ammonia (sp.gr. 0.9 g/ml). The reaction was carried out in an ice-bath. About 20 ml of ethanol was then added to precipitate out a white crystalline compound. The product was isolated by suction filtration followed by washing 3 or 4 times with ethanol; yield 1.8 g (84%). [Found: H, 5.12; N, 13.62; As, 35.37; O_2^{2-} , 15.42. Req'd. for $(\text{NH}_4)_2[\text{AsO}_3(\text{OOH})]\cdot\text{H}_2\text{O}$: H, 5.24; N, 13.34; As, 35.69; O_2^{2-} , 15.23%]. Λ_M (H_2O): $250 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. IR (KBr, cm^{-1}): 416 (s), 790 (s), 835 (s), 1469 (m), 1640 (s), 3510 (s, br). Laser Raman (KBr, cm^{-1}): 418, 787, 838.

Ammonium tetraoxodifluoro- μ -peroxodiarsonate(V) hexahydrate $(\text{NH}_4)_2[\text{As}_2\text{O}_4(\text{O}_2)\text{F}_2]\cdot 6\text{H}_2\text{O}$ (**2**)

To a mixture of As_2O_3 (1 g, 5.1 mmol) and NH_4F (0.3 g, 8.11 mmol) was added 3 ml of 48% HF (72.0 mmol). To this was then added 15 ml of 30% H_2O_2 (132.35 mmol), when a slurry was obtained. The pH of the reaction solution was then raised slowly by dropwise addition of aqueous ammonia until the mixture became clear. The pH of the solution recorded at this stage was found to be 9. The reaction was conducted at ice-bath temperature. About 25 ml of ethanol was added to bring about precipitation of the title compound. This was isolated by suction filtration and dried in vacuo over conc. H_2SO_4 ; yield 1.5 g (69.5%). [Found: H, 4.58; N, 6.51; As, 35.2; O_2^{2-} , 7.34; F^- , 8.13. Req'd. for

$(\text{NH}_4)_2[\text{As}_2\text{O}_4(\text{O}_2)\text{F}_2] \cdot 6\text{H}_2\text{O}$: H, 4.67; N, 6.54; As, 35.03; O_2^{2-} , 7.47, F^- , 8.88%. IR (KBr, cm^{-1}): 385 (m), 413 (s), 735 (s), 795 (s), 820 (m), 1460 (m), 3515 (s, br).

Reactions of **1** and **2** with some selected organic substrates

The reactions have been conducted under N_2 atmosphere.

Transformation of salicylaldehyde to catechol

To salicylaldehyde (8.19 mmol), an aqueous solution (25 ml each) of either **1** (12.24 mmol) or **2** (12.27 mmol) was added with stirring. The solution temperature rose to $\sim 50^\circ\text{C}$ and a dark colour developed. Stirring was continued for $\sim 6\text{h}$ and then allowed to stand overnight. The solution was neutralised with acetic acid and evaporated to dryness and the residue was treated with toluene ($5 \times 10\text{ ml}$). The toluene fraction was dried by sodium sulphate treatment which upon evaporation gave catechol (mp. $103\text{--}104^\circ\text{C}$); yield 0.4 g (44.4%).

Transformation of benzonitrile to benzamide

Benzonitrile (9.71 mmol) was mixed with 15 ml of ethanol and to this was added an aqueous solution (30 ml each) of either **1** (14.53 mmol) or **2** (14.54 mmol). The reaction solution was stirred for 3h at $\sim 50^\circ\text{C}$. The mixture was then cooled to room temperature and treated with chloroform ($3 \times 15\text{ ml}$). The combined organic layers were washed with water, dried over sodium sulphate and concentrated to give crude benzamide which was purified by recrystallisation from chloroform (mp. $130\text{--}131^\circ\text{C}$); yield 0.6 g (51.1%).

Transformation of benzil to benzoic acid

An acetonitrile (15 ml) solution of benzil (4.75 mmol) was mixed with an aqueous solution (30 ml each) of **1** (7.09 mmol) or **2** (7.13 mmol) and the mixture was refluxed for $\sim 1\text{h}$. The reaction mixture was poured into ice-cold water (50 ml). Any unreacted benzil separated as yellow solid was filtered off. The filtrate was acidified with HCl and then treated with chloroform ($4 \times 20\text{ ml}$), dried over sodium sulphate and concentrated to obtain benzoic acid. The crude product was purified by recrystallisation from chloroform (mp. $120\text{--}121^\circ\text{C}$); yield 0.6 g (51.6%).

Reaction of **1** with SO_2

A slow stream of SO_2 gas was bubbled through the solution of **1** with gentle stirring. An immediate reaction took place. The flow of the substrate

gas was continued until the product isolated from a small amount of the solution was found to be devoid of peroxide. The solution was then concentrated by slow evaporation. On cooling to ambient temperature, a white crystalline product was obtained. The compound was identified to be $(\text{NH}_4)_3[\text{AsO}_2(\text{SO}_4)]$.

Arsenic^{5a}, fluoride^{5b}, active oxygen (O_2^{2-})^{5c} and sulphate^{5d} contents were determined following literature methods. The metal to active oxygen stoichiometries were checked by gas-volumetric analyses. Microanalytical data were obtained from the microanalytical laboratory, Department of Chemistry, North-Eastern Hill University, Shillong.

Results and discussion

It is known from literature² that combination of arsenic oxides and hydrogen peroxide brings about a variety of oxidations. This points to the involvement of peroxyarsenate intermediates in the processes. Arsenic(III) is also known to affect the decomposition of H_2O_2 (ref. 6) indicating the possibility of oxidation of As(III) to As(V). Considering these, our first concern was to ascertain an appropriate condition for the oxidation of arsenic(III). For this, known amounts of As_2O_3 were allowed to react with excess of hydrogen peroxide separately at different pH values. This was followed by iodometric determination of arsenic(V) content, after removing the unreacted H_2O_2 by boiling with dil. HCl solution. By this process it was ascertained that trivalent arsenic was oxidised quantitatively to its pentavalent state at pH 9-9.5. It is relevant to mention that for their kinetic studies, Nishida and Kimura⁷ found that arsenic(III) was oxidised to arsenic(V) by peroxodisulphate ion in alkaline solution of pH > 8.6. It has now been possible to show that in alkaline solution (pH 9-9.5), arsenic(III) oxide can be reacted with an excess of 30% H_2O_2 leading to the formation of a peroxyarsenate(V), $(\text{NH}_4)_2[\text{AsO}_3(\text{OOH})] \cdot \text{H}_2\text{O}$ (**1**). This success prompted us to synthesise fluoroperoxy-arsenate(V). Since arsenic is known to form stable compounds with fluoride, it was anticipated that in the presence of both peroxide (O_2^{2-}) and fluoride, the latter might simultaneously coordinate with arsenic(V). The synthesis of $(\text{NH}_4)_2[\text{As}_2\text{O}_4(\text{O}_2)\text{F}_2] \cdot 6\text{H}_2\text{O}$ (**2**) has been accomplished from the reaction of As_2O_3 with 30% H_2O_2 in the presence of 48% HF and NH_4F at pH 9. It is apparent that H_2O_2 indeed played at least two important roles in the synthesis, i.e., to

oxidise As(III) to As(V) and to provide peroxide or hydroperoxide for coordination to As(V) centre.

Both the compounds are white crystalline products. In water, decomposition of **1** has been found to be rather slow whereas **2** decomposes relatively fast with the loss of active oxygen. Accordingly, solution electrical conductance measurement could be made only with compound **1**. The compounds do not seem to be hygroscopic, however, they are not very stable if kept exposed to air for more than ~ 5 h. They suffer a loss of active oxygen content to the extent of 4 or 5% in a span of 24 h. But, they can be stored in sealed ampoules for several days. The peroxoarsenates decompose in the presence of sulphuric acid liberating H_2O_2 quantitatively thereby rendering it easy to determine the active oxygen contents in the compounds. The chemical determination of active oxygen in such compounds is considered to be of extreme importance. This was accomplished by titration with standard KMnO_4 solution in the presence of boric acid to prevent any loss of active oxygen. The results of chemical determination of active oxygen and arsenic present in the compounds suggested the occurrence of As : O_2^{2-} for **1** and **2** in 1 : 1 and 2 : 1 ratios, respectively. The metal to active oxygen stoichiometries were also ascertained by gas-volumetric analyses^{5e}.

Each of the two compounds exhibited characteristic spectral features in the infrared region. Important among the bands for **1** are those observed at 790s ($\nu_{\text{As}=\text{O}}$) 416s (As = O, deformation) (refs 8a, 9) and 835s cm^{-1} ($\nu_{\text{O}-\text{O}}$) (ref. 10). Complimentary bands at 787, 418, and 838 cm^{-1} owing to $\nu_{\text{As}=\text{O}}$, deformation mode of As = O, and $\nu_{\text{O}-\text{O}}$, respectively, were also observed in the laser Raman spectrum of the compound. Quite significant is the appearance of a medium intensity peak at 1469 cm^{-1} in the IR spectrum of **1**. This has been assigned to the ^-OOH deformation mode¹⁰, thus attributing to the occurrence of hydroperoxide (^-OOH) bonded to an As(V) centre. It may be noted that the presence of an O_2^{2-} , instead of an ^-OOH , would require the complex to be a 3 : 1 electrolyte, however, the solution electrical conductance of a 10^{-3} M solution of the compound ($250 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$), recorded for a solution of a freshly prepared sample, clearly points to a 2 : 1 type electrolytic species. Similarly, the N : As ratio would be either 1 : 1 or 1 : 3, instead of 2 : 1 as obtained from chemical analyses, if the compound were a perhydrate [for instance $\text{NH}_4\text{AsO}_3 \cdot \text{H}_2\text{O}_2$ or $(\text{NH}_4)_3\text{AsO}_4 \cdot \text{H}_2\text{O}_2$]. These provide additional support to the formulation of

compound **1**. The IR absorption bands at 1640(s) and 3510(s,br) cm^{-1} correlate well with the occurrence of an uncoordinated^{8b} water.

The infrared spectrum of **2** is in agreement with the postulated structure. The significant features involve absorptions at 795(s) and 413(s) cm^{-1} originating from $\nu_{\text{As}=\text{O}}$ and As = O deformation, respectively, at 735(s) and 385(m) cm^{-1} attributable to As-F stretching and deformation modes^{8c} respectively, and at 820(m) cm^{-1} due to the stretching frequency of peroxide¹⁰. The presence of a medium intensity broad band at 820 cm^{-1} and the absence of ν_2 and ν_3 modes of a chelated type coordinated peroxide suggest that O_2^{2-} in **2** occurs as a bridging ligand. Unfortunately, owing to an extensive fluorescence, this compound did not provide a satisfactory Raman spectrum. The absence of any absorption at $\sim 1460 \text{ cm}^{-1}$ in its IR spectrum is a clear indication of the absence of hydroperoxide (^-OOH), unlike in case of **1**. The patterns arising from NH_4^+ and uncoordinated water were unambiguous.

Compounds **1** and **2** were separately reacted with each of the following organic substrates, namely, salicylaldehyde, benzonitrile, and benzil (vide Experimental). The compounds reacted very effectively transforming salicylaldehyde to catechol, benzonitrile to benzamide, and benzil to benzoic acid.

In addition to the afore mentioned oxidative organic transformations, the reaction between $\text{SO}_2(\text{g})$ and a peroxoarsenate(V) was also conducted. The main concern here was to improvise a soft synthetic methodology for arsenic(III) sulphates. Such compounds are difficult to obtain since the literature procedures involve stringent experimental conditions owing to the use of oleum containing varying concentration of SO_3 (ref. 11). In the present studies, $(\text{NH}_4)_2[\text{AsO}_3(\text{OOH})] \cdot \text{H}_2\text{O}$ (**1**) was reacted with $\text{SO}_2(\text{g})$ (vide Experimental). A very facile reaction took place affording $(\text{NH}_4)_3[\text{AsO}_2(\text{SO}_4)]$ as the product. This was characterised by chemical analyses and vibrational spectroscopy. Therefore, it is clear that the reaction provides an easy access to the sulphato compound of the metal.

Acknowledgement

We thank the UGC, New Delhi, for the award of a fellowship (GCM) and for financial assistance to the Department of Chemistry (NEHU) under the UGC Special Assistance Program.

References

- 1 Dymova Z N & Bogdona G A, (*Mosk Tekstil Inst Moscow*) *Izv Vyssh Ucheb Ziaved Khim Khim Tekhnol*, 10(9) (1967) 1010; (Russ), *Chem Abstr*, 68 (1968) 45709h.
- 2 McMullen C H, *Ger Offen*, 2 607, 768 (Cl. CO7D301/12), 09 Sep. 1976, US App., 583, 27 Feb. 1975, 23pp; (*Chem Abstr*, 86 (1977) 29606p); Grasselli R K & Friederich S M, Shaw G W & Hardman F H, *Ger Offen*, 1, 808, 990, US 3, 544, 616 (Cl. 260-465, 3, CO7C) (*Chem Abstr*, 1 (1969) 112453x); Kamimura S, Maki T & Minode K, Japan 69, 13, 684 (Cl. 16B6) 19 June 1969, Appl. 17 Oct, 1966, 2pp (*Chem Abstr*, 71 (1961) 112502n).
- 3 Chaudhuri M K & Ghosh S K, *Inorg Chem*, 21 (1982) 4020; 23 (1984) 534; Bhattacharjee M N, Chaudhuri M K & Islam N S, *Inorg Chem*, 28 (1989) 2420 and references therein; Bhattacharjee C R & Chaudhuri M K, *J chem Soc, Dalton Trans*, (1992) 2943 and references therein; Ravishankar H N, Chaudhuri M K & Ramasarma T, *Inorg Chem*, 33 (1994) 3788.
- 4 Bhattacharjee C R, Bhattacharjee M, Chaudhuri M K & Chaudhuri S, *Polyhedron*, 9 (1990) 1653.
- 5 Vogel A I, *A text book of quantitative inorganic analysis*, 4th Edn (Longman, Green, London) 1978, (a) p.367; (b) p.269; (c) p.363; (d) p. 462; (e) p. 1090.
- 6 Levi G R & Ghiron D, *Atti Accad Linci*, 21 (1935) 454; *Chem Abstr*, 29 (1935) 7848.
- 7 Nishida S & Kimura M, *J chem Soc, Dalton Trans*, (1989) 357.
- 8 Nakamoto K, *Infrared and Raman spectra of inorganic and coordination compounds*, 4th Edn (Wiley, New York) 1986, (a) p.138; (b) p.228; (c) p.150.
- 9 Siebert H, *Z anorg allg Chem*, 275 (1954) 225.
- 10 Jones D P & Griffith W P, *J chem Soc, Dalton Trans*, (1980) 2526.
- 11 Mercier R & Douglade J, *Acta Crystallogr, B*, 38 (1982) p.720; p.896; p.1731. *Comprehensive coordination chemistry*, Vol 3, edited by G Wilkinson (Pergamon Press, Oxford) 1987, p.246.