SYNTHESIS AND SPECTRAL STUDIES OF STRUCTURE OF POSSIBLE COMPOSITION OF IODINE OXIDE PARTICLES FORMED IN THE ATMOSPHERE

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Iodine oxide nanoparticles were generated photochamically from I_2 in the presence of O_3 in the atmosphere. The possible compounds I_2O_4 and I_2O_5 formed were synthesized in the laboratory and their compositions were studied by UV- Visible spectrometer and analyzed Flash combustion method using a Thermo Flash EA 1112 series. The elemental analysis shows I_2O_4 is possible stable compounds in the atmosphere. I_2O_4 is insoluble in water and may be atmospherically relevant to act as ice nuclei in the atmosphere. Although, the spectral studies show that iodine forms I_3^- and I^- ions in ethanol and both I_2O_5 and I_2O_4 show similar trends to iodine but the molar extinctions are not equal. Also I_2O_5 is observed between 250-400nm while I2O4 does not show any absorbance in this region.
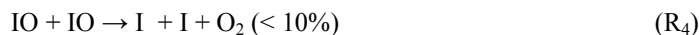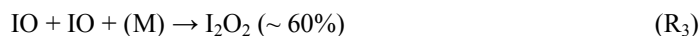
INTRODUCTION

Iodine oxide nanoparticles form from homogeneous nucleation in coastal areas when CH_2I_2, CH_3I, and I_2 etc are photolysed in the presence of an oxidizing agent O_3 (Jimenez et al., 2003; McFiggans et al., 2004; Saunders and Plane, 2005). However, uncertainty remains in the formation pathway of particles and the composition of the resulting particles. Initially, the precursor gas photolysis and the resulting iodine atoms react with ozone (O_3) to produce iodine monoxide (IO):

$$RI \text{ or} I_2 +hv \rightarrow I +O_3 \rightarrow IO+O_2 \qquad (R_1)$$

where, R is an organic fragment. The self reaction of IO then proceeds via at least three pathways (Bloss et al., 2001; Kaltsoyannis and Plane, 2008):
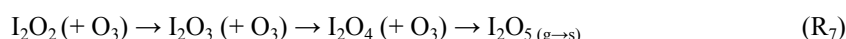
$$IO + IO \rightarrow OIO + I \ (\sim 40\%) \qquad (R_2)$$

$$IO + IO + (M) \rightarrow I_2O_2 \ (\sim 60\%) \qquad (R_3)$$

$$IO + IO \rightarrow I \ + I + O_2 \ (< 10\%) \qquad (R_4)$$

I_2O_2 is probably thermally unstable around 290 K and decomposes to OIO + I. Then, as a result of the self reaction of OIO, or the recombination of IO and OIO produces the following polymers (Kaltsoyannis and Plane, 2008):

$$IO + OIO (+ M) \rightarrow I_2O_3 \qquad (R_5)$$

$$\text{OIO + OIO (+M)} \rightarrow I_2O_4 \tag{R_6}$$

The formation of the stable higher iodine oxides such as I_2O_5 could occur through a series of oxidation reactions of iodine oxide with ozone (R_7) in the gas phase, before polymerizing to form solid particles of pure I_2O_5. However, (R_5) may be in competition with polymerization reactions (R_8) of I_2O_2, I_2O_3, and I_2O_4 molecules, leading to particles of mixed composition where the O/I ratio is less than 2 i.e. $I_2O_{\leq 4}$ (Saunders and Plane, 2005):

$$I_2O_2 (+ O_3) \rightarrow I_2O_3 (+ O_3) \rightarrow I_2O_4 (+ O_3) \rightarrow I_2O_{5\ (g \rightarrow s)} \tag{R_7}$$

$$I_2Ox + IyOz \rightarrow I_2 + yOx + z_{\ (g \rightarrow s)} \tag{R_8}$$

where x =2-4, y=1or2 and z=1-4

The identification of the presence of iodine within the ultrafine aerosol particles which regularly form in the huge numbers ($>10^6$ cm^{-3}) in marine boundary layer (MBL) at seaweed-rich coastal areas is most readily explained by the following scenario (Mäkelä *et al.*, 2002; O'Dowd and Hoffmann, 2005). The release of iodine containing gases (*i.e.* I_2 and CH_2I_2) from macro-algae during day time low tide periods brings about the photolytic production of reactive iodine atoms which are rapidly oxidised by O_3. This lead to the formation of gas phase iodine oxide particles such as IO and OIO which, through further reaction/polymerization routes, lead to the formation of higher iodine oxide particles which is shown below (Mäkelä *et al.*, 2002; Saunders and Plane, 2005).
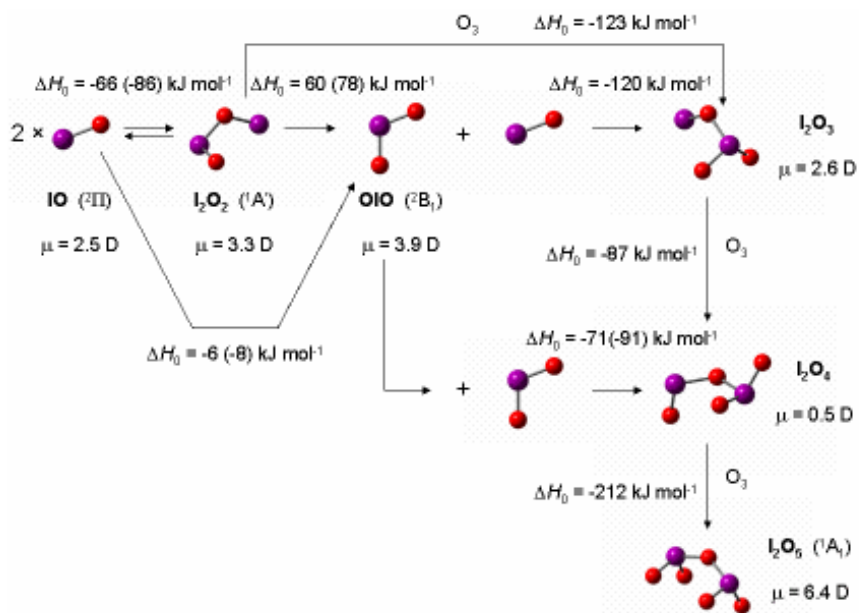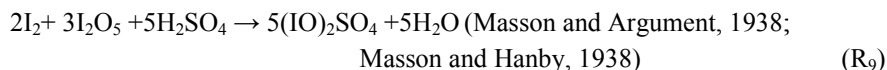

Fig. 1. The possible formation pathways of iodine oxides up to I_2O_5 from IO and their optimised geometries (the figure is adapted from Saunders and Plane, 2005).

Synthesis of I_2O_4

In order to study spectral studies and analysis of composition of these compounds, a number of possible particle compositions must be considered bearing in the mind that water and sulpuric acid uptake form by the iodine oxide particles forms Iodosyl Sulphate (Saunders *et al.*, 2010). Thus, Out of possible composition of iodine oxide particles (I_2O_4 or I_2O_5), I_2O_4 has been done synthesized in the laboratory including the following iodosyl sulphate [(IO)$_2$SO$_4$] species of iodine as they are not commercially available.

Synthesis of Iodosyl Sulphate, [(IO)$_2$SO$_4$] and I$_2$O$_4$

The synthesis of [(IO)$_2$SO$_4$] and I$_2$O$_4$ were carried out the laboratory according the following reactions;

$$2I_2 + 3I_2O_5 + 5H_2SO_4 \rightarrow 5(IO)_2SO_4 + 5H_2O \text{ (Masson and Argument, 1938;}$$

$$\text{Masson and Hanby, 1938)} \qquad (R_9)$$

OR

$$2I_2 + 6NaIO_3 + 11H_2SO_4 \rightarrow 5(IO)_2SO_4 + 6NaHSO_4 + 8H_2O \text{(Beringer } \textit{et al}., 1953) \qquad (R_{10})$$

In the above reactions R$_9$ and R$_{10}$, powders of iodine and iodine pentoxide were mixed together and then concentrated sulphuric acid added slowly. The reaction mixture was vigorously stirred for 24-48 hrs. Initially a brown solution is obtained which converts into a yellow precipitate of iodosyl or *Chretien's* sulphate on continued stirring.
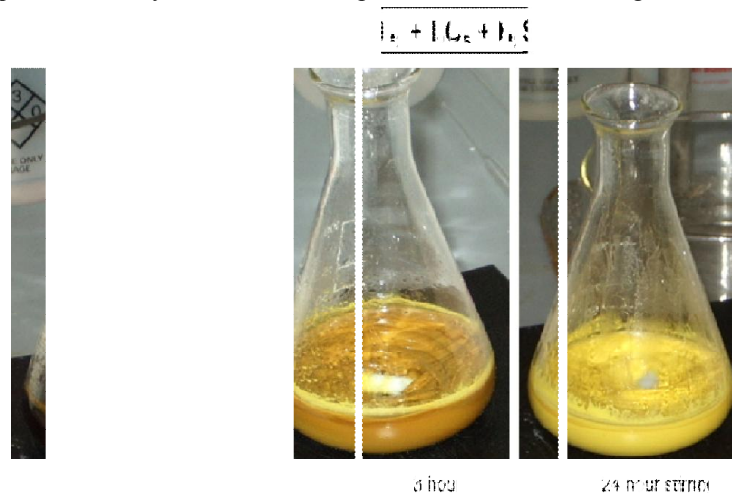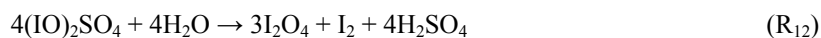

Fig. 2. Photograph of the various stages in the attempted preparation of iodosyl sulphate

According to reaction R$_9$, only water is eliminated with iodosyl sulphate. So, the pH of the liquid left in the reaction should be 7 i.e. neutral. This is an indication for completion of the reaction but, the H$_2$SO$_4$ was taken in excess amount. So the pH of the liquid always remains less than 7 i.e. the liquid remains acidic. So, it is not possible to filter the precipitate using filter paper as this is burnt rapidly. To overcome this problem, the filtration process is carried out by using a sintered glass funnel. In this process the yellow precipitate remains yellow while liquid remains in the funnel but the precipitate changes colour when all liquid is eliminated from the precipitate. The yellow precipitate changes first into a brown colour and finally into a grey colour. This indicates that the prepared sulphate is very unstable and decomposes to iodine and iodic acid with back reaction of water vapour.
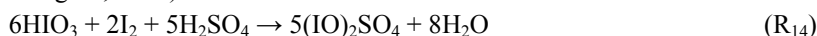
$$5(IO)_2SO_4 + H_2O \rightarrow 2I_2 + 6HIO_3 + 5H_2SO_4 \qquad (R_{11})$$

OR

$$4(IO)_2SO_4 + 4H_2O \rightarrow 3I_2O_4 + I_2 + 4H_2SO_4 \qquad (R_{12})$$

Since water is eliminated R$_9$ and R$_{10}$, it may be possible that the iodosyl sulphate is converted into I$_2$O$_4$ because I$_2$O$_4$ is also yellow in colour which is stable. It does not react with moist air but in excess of water it decomposes into iodic acid and iodine.

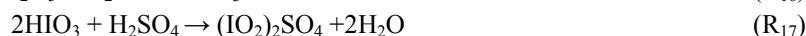$$5I_2O_4 + 4H_2O \rightarrow I_2 + 8HIO_3 \qquad (R_{13})$$

It is possible to isolate the yellow precipitate in stable form when it is washed with acetic acid to eliminate the sulphuric acid from the precipitate then the yellow colour remains. After drying the precipitate is washed with water to obtain a fine powder (Ziegler and Marr, 1962).

I_2O_4 may also be generated through the reaction of HIO_3 with concentrated H_2SO_4 and iodine (Bahl and Partington, 1935).

$$6HIO_3 + 2I_2 + 5H_2SO_4 \rightarrow 5(IO)_2SO_4 + 8H_2O \qquad (R_{14})$$

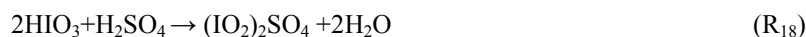$$4(IO)_2SO_4 + 4H_2O \rightarrow 3I_2O_4 + I_2 + 4H_2SO_4 \qquad (R_{15})$$

In this method the same procedure as above was applied. Washing with acetic acid and water a fine yellow stable powder was obtained.

Synthesis of Iodyl Sulphate $[(IO_2)_2SO_4]$ /Iodyl Hydrogen Sulphate $[IO_2HSO_4]$

$$I_2O_5 + H_2O \rightarrow 2HIO_3 \qquad (R_{16})$$

$$2HIO_3 + H_2SO_4 \rightarrow (IO_2)_2SO_4 + 2H_2O \qquad (R_{17})$$

OR

$$2HIO_3 + H_2SO_4 \rightarrow (IO_2)_2SO_4 + 2H_2O \qquad (R_{18})$$

In the above reactions a stoichiometric amount of I_2O_5/HIO_3 is dissolved in water according to their solubility and then sulphuric acid is added slowly. This is a very slow reaction. On leaving for a day at room temperature some transparent fine white crystals are obtained. These crystals are soluble in water. These crystals may be of Iodyl/Iodosyl hydrogen sulphate (Gillespie and Senior, 1964).

$$HIO_3 + 2H_2SO_4 \rightarrow IO_2HSO_4 + H_3O^+ + HSO_4^- \qquad (R_{19})$$

OR

$$HIO_3 + H_2SO_4 \rightarrow IO_2HSO_4 + H_2O \qquad (R_{20})$$

However, the reaction occurs rapidly if an excess of sulphuric acid is added to the solution of I_2O_5/HIO_3 in water. A white precipitate soluble in water is obtained. It may also be Iodyl/Iodosyl hydrogen sulphate.

Elemental Analysis of Synthesised compounds

All powders/crystals obtained in the reactions described above were analyzed to determine the % of element present in each compound. C, H, N, O, and S were analysed by Flash combustion method using a Thermo Flash EA 1112 series and halogens were analysed by Oxygen Flask combustion method. All samples were analysed with standard ±0.3% accuracy. The elemental analysis results are matched with theoretical percentage for I_2O_4 which was prepared by all three methods i.e. R_9, R_{10}, and R_{14} (sulphate and hydrogen sulphate powders were not submitted for elemental analysis). The very good agreement between the determined and theoretical elemental composition of the powders (1-3 in Table 3) indicate that I_2O_4 is the final product of reactions R_9, R_{10}, and R_{14}.

Table 1. The table shows the theoretical and analysed elemental percentage of synthesised I_2O_4

S.N.	Reaction	Final Product	Theoretical (%)	Analyzed (%)
1	$2I_2 + 3I_2O_5 + 5H_2SO_4$	I_2O_4	I = 79.9 O = 20.1	I = 77.25 ± 0.3 O = 19.15 ± 0.3
2	$2I_2 + 6NaIO_3 + 11H_2SO_4$	I_2O_4	I = 79.9 O = 20.1	I = 76.3 ± 0.3 O = 20.35 ± 0.3
3	$6HIO_3 + 2I_2 + 5H_2SO_4$	I_2O_4	I = 79.9 O = 20.1	I = 77.5 ± 0.3 O = 19.25 ± 0.3

The percentage of I_2O_4 is very close to theoretical values. The difference between theoretical and analysis values may be due to $\pm 0.3\%$ uncertainty in analysis and compounds which used in synthesis are not 100% pure. The purity of these compounds is as follows:

Table 2: The table shows percentage purity of I_2O_5, I_2, HIO_3, and H_2SO_4

I_2O_5	I_2	HIO_3	H_2SO_4
98%	99.5%	99.5%	98%

The elemental analysis confirmed that only I_2O_4 is possible stable compounds. I_2O_4 is not soluble in water. I_2O_4 may be atmospherically relevant and may act as ice nuclei. However, I_2O_5 and HIO_3 are soluble in water so these may show deliquescence/ efflorescence.

Spectral Analysis of I_2O_4, I_2O_5, I_2, and HIO_3

Although I_2O_4 was confirmed by elemental analysis, a spectral analysis was also performed to further identification. For UV-Visible spectra of I_2O_4, I_2O_5, I_2, and HIO_3, the UV-Visible spectra were taken using UV-Visible Spectrometer, model Perkin Elmer-Lamda 900 with 1 nm slit. The UV-Visible Spectra of I_2O_4, I_2 were taken from solutions in ethanol because these compounds are very sparingly soluble in water and the spectra of HIO_3 was taken only in water since these are not soluble in ethanol. Spectra of I_2O_5 were taken in both ethanol and water. The IR spectra were taken directly from the solid samples.
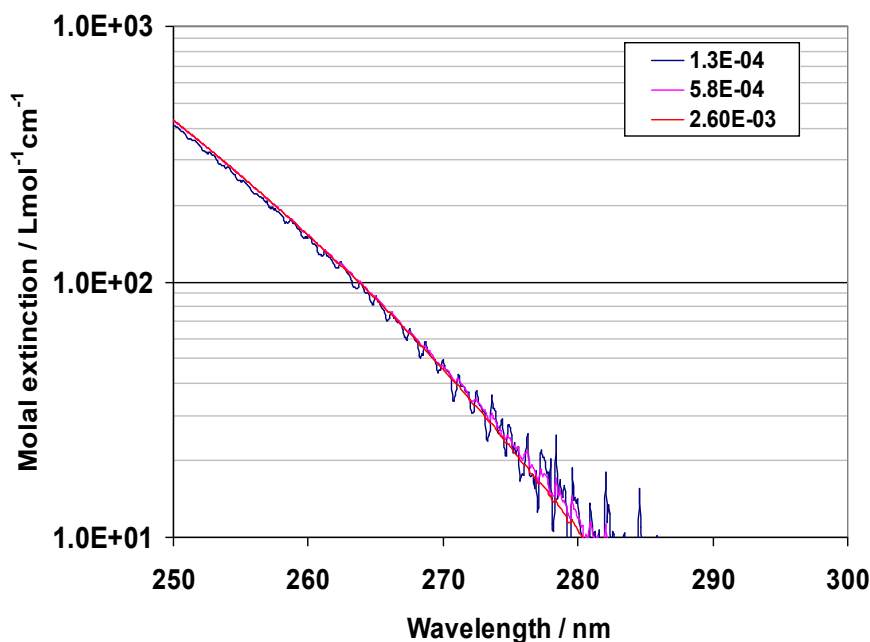

Fig. 3. UV-Visible Spectra of I_2O_5 in water (solution concentrations in moles L^{-1} are indicated in the panel).
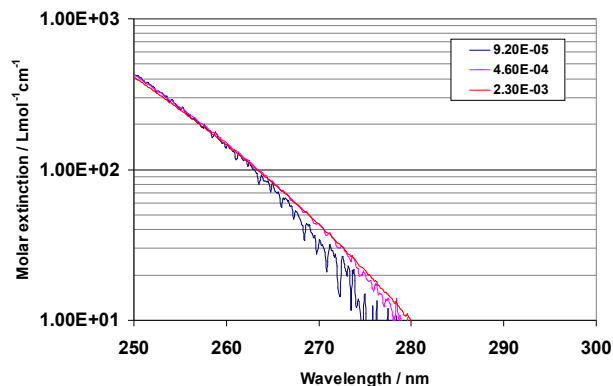
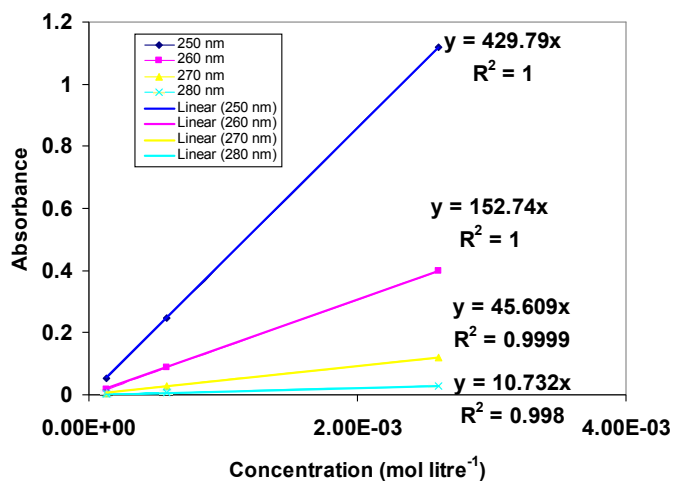**Fig. 4. UV-Visible Spectra of HIO$_3$ in water (solution concentrations in moles L^{-1} are indicated in the panel).**

Fig. 5. Variation of measured absorbance with concentration of I$_2$O$_5$ in water

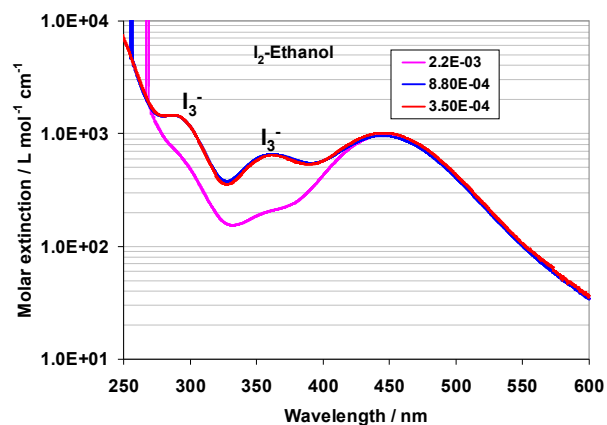**Fig. 6. UV-Visible spectra of I$_2$ in ethanol (solution concentrations in moles L^{-1} are indicated in the panel).**
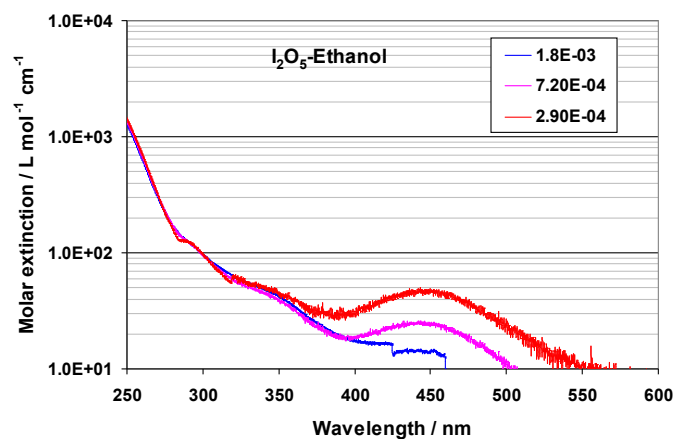
Fig. 7. UV-Visible spectra of I_2O_5 in ethanol (solution concentrations in moles L^{-1} are indicated in the panel).
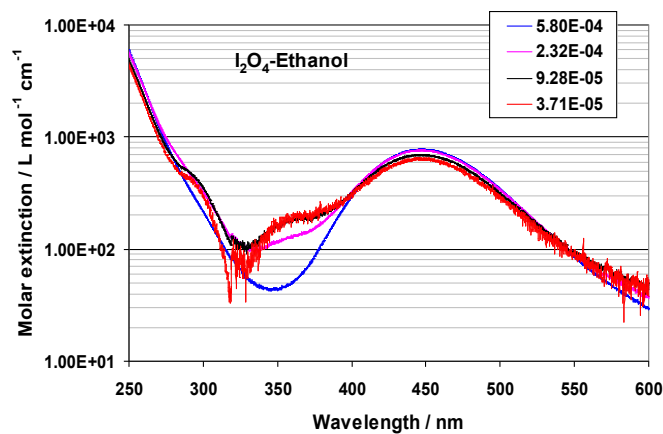
Fig. 8. UV-Visible spectra of I_2O_4 in ethanol (solution concentrations in moles L^{-1} are indicated in the panel).
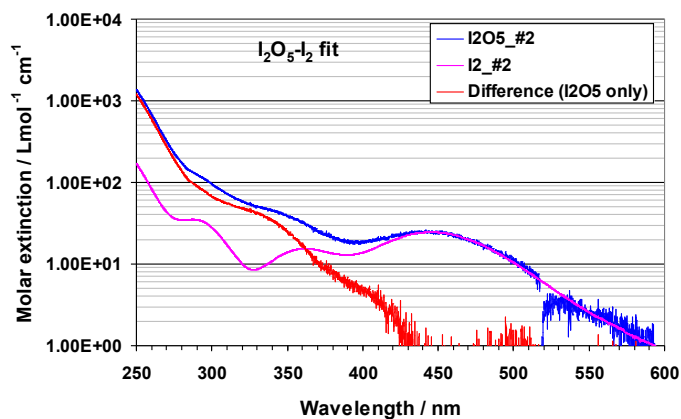
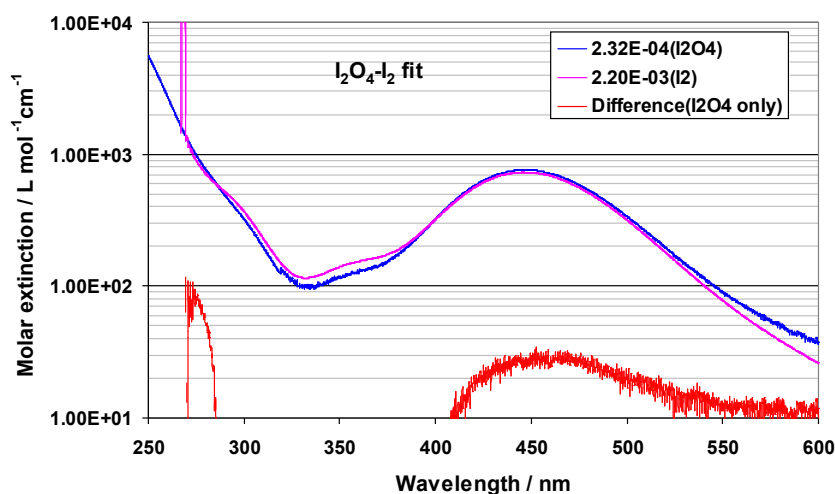**Fig. 9.** UV-Visible spectra of I_2O_5 (I_2 contribution fitted and subtracted out-red line)

Fig. 10. UV-Visible spectra of I_2O_4 (I_2O_5 (I_2 contribution fitted and subtracted out-red line).

CONCLUSIONS

Figures 3-4 confirm that for all compounds the molar extinction is independent of the solution concentration. These spectra show that all three compounds i.e. I_2O_5 and HIO_3 give the IO_3^- ion in solution. Figure 5 shows the absorbance increases linearly with concentration of the I_2O_5 and HIO_3 solutions. This means that all solutions obey the Beer-Lambert law and the molar extinction of I_2O_5 and HIO_3 are the same because I_2O_5 forms HIO_3 with water (Chase, 1996).

$$1/2 I_2O_5 + 1/2\ H_2O \rightarrow HIO_3 \tag{R_{21}}$$

Figures 6-8 show the spectra of I_2, I_2O_5, and I_2O_4 in ethanol and figures 9-10 show fits of I_2O_5-I_2 and I_2O_4-I_2 spectra. The spectra of iodine show that iodine forms I_3^- and I^- ions in ethanol(Batley, 1928). From figures 7 and 8 it was observed that both I_2O_5 and I_2O_4 show similar trends to iodine but the molar extinctions are not equal for different concentrations. This may be due to both I_2O_5 and I_2O_4 reacting with ethanol to form I^- ion and subsequently I_2. From figures 7 and 10 it is clear that I_2O_5 is observed between 250-400nm while I2O4 does not show any absorbance in this region. The following reactions are possible from these compounds with ethanol (Batley, 1928; Pechtl et al., 2007).

$$C_2H_5OH + I_2/\ I_2O_5/I_2O_4 \rightarrow CH_3CHO + 2HI \tag{R_{22}}$$

$$HI + I_2 <-> HI_3 \tag{R_{23}}$$
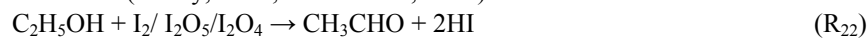
The oxidation of HI and HI_3 may also be considered
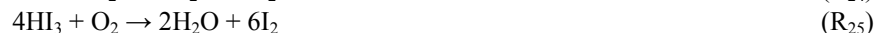
$$4HI + O_2 \rightarrow 2H_2O + 2I_2 \tag{R_{24}}$$

$$4HI_3 + O_2 \rightarrow 2H_2O + 6I_2 \tag{R_{25}}$$

ACKNOWLEDGEMENTS

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