

Short Communication

# Thermal Decomposition of $(\text{IO})_2(\text{SO}_4)_{1-x}(\text{SeO}_4)_x$

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Different aspects of the quasi-reversible cycle  $\text{I}_2\text{O}_5 \rightarrow (\text{IO})_2(\text{SO}_4)_{1-x}(\text{SeO}_4)_x \rightarrow \text{I}_2\text{O}_4 \rightarrow \text{I}_2\text{O}_5$  have been considered in two recent communications by the authors.<sup>1,2</sup> At the time these articles were prepared, we were not aware that there also exists another quasi-reversible cycle,  $\text{I}_2\text{O}_5 \rightarrow (\text{IO})_2(\text{SO}_4)_{1-x}(\text{SeO}_4)_x \rightarrow \text{I}_2\text{O}_5$ , among the involved phases.

Samples of  $(\text{IO})_2(\text{SO}_4)_{1-x}(\text{SeO}_4)_x$  were synthesized and characterized as described in Ref. 1. Thermogravimetric (TG) measurements were made between 20 and 500 °C with a Perkin-Elmer 7 series thermal analysis system using 25–45 mg samples and a heating rate of 10 °C min<sup>-1</sup>.

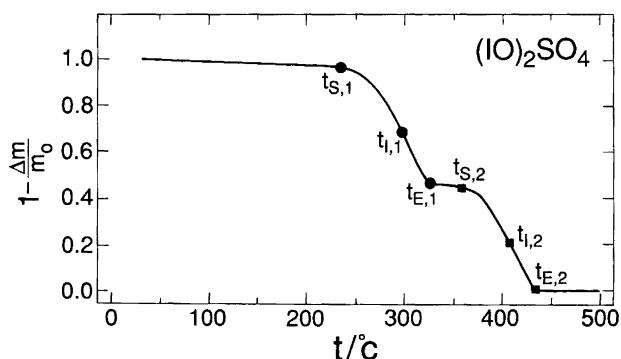
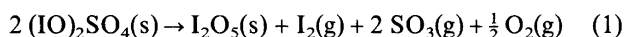


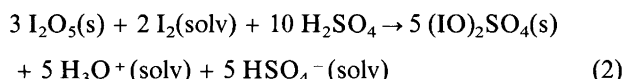
Fig. 1. TG curve for  $(\text{IO})_2\text{SO}_4$ . Start ( $t_s$ ), inflection ( $t_i$ ) and end ( $t_e$ ) temperatures are approximately 235, 300 and 320 °C for step 1 and 355, 415 and 435 °C for step 2. Calculated weight loss parameter  $(1 - \Delta m/m_0)$  for step 1 according to eqn. (1) is 0.437; the observed value is 0.446.

TG data for a well prepared and preserved sample of  $(\text{IO})_2\text{SO}_4$  are given in Fig. 1. The results show that the thermal decomposition occurs in two steps, the first in the temperature interval 235–320 °C and the second between 355 and 435 °C. The characteristic temperatures ( $t_s$ ,  $t_i$

and  $t_e$  for the start, inflection and end point, respectively) for step 2 suggest immediately (see Ref. 3) that  $\text{I}_2\text{O}_5$  is formed as an intermediate decomposition product of  $(\text{IO})_2\text{SO}_4$ . This was ascertained from powder X-ray diffraction data collected for the remains of the samples after decomposition at 325 °C. TG isotherms at 325 °C show that  $\text{I}_2\text{O}_5$  sublimates (cf., e.g., Ref. 4) at a rate of 0.024 mg min<sup>-1</sup>, a feature which, *inter alia*, contributes to a non-horizontal curve section between  $t_{e,1}$  and  $t_{s,2}$  in Fig. 1. Comparison of observed (0.446) and calculated (0.437) values for the weight loss ( $\Delta m$ ) parameter  $(1 - \Delta m/m_0)$  shows that the partial thermal decomposition of  $(\text{IO})_2\text{SO}_4$  in step 1 takes place according to reaction (1):

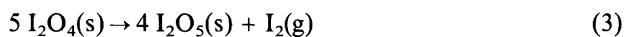


This is recognized as the quasi-reverse reaction to that for the synthesis of  $(\text{IO})_2\text{SO}_4$  in concentrated sulfuric acid:<sup>1</sup>



The different relative amounts of  $\text{I}_2$  and  $\text{I}_2\text{O}_5$  in eqns. (1) and (2) reflect the fact that the redox process according to eqn. (1) also involves one of the oxygen atoms.

Care has to be taken during synthesis and all subsequent handling of  $(\text{IO})_2\text{SO}_4$  in order to obtain the good fit quoted above between observed and calculated weight loss. A usual outcome, with rapid handling, but without inert atmosphere treatment, is  $(1 - \Delta m/m_0)_{\text{obs}}$  around 0.5. The cause of the problem is the highly hygroscopic nature of  $(\text{IO})_2\text{SO}_4$  (cf., e.g., Ref. 5), which starts the conversion into  $\text{I}_2\text{O}_4$  immediately after exposure to moist air. Although  $\text{I}_2\text{O}_4$  also undergoes thermal decomposition into  $\text{I}_5\text{O}_5$  (at 215–260 °C):<sup>3</sup>



the contamination of  $(\text{IO})_2\text{SO}_4$  by  $\text{I}_2\text{O}_4$  invariably leads to a value for  $(1 - \Delta m/m_0)_{\text{obs}}$  that is too high.

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The hygroscopic behaviour of  $(\text{IO})_2(\text{SO}_4)_{1-x}(\text{SeO}_4)_x$  increases with increasing selenate content ( $x$ ), and the contamination problems consequently become more severe. The 'signature' of  $\text{I}_2\text{O}_4$  (see Ref. 3) is, e.g., clearly visible in the TG curves for  $(\text{IO})_2(\text{SO}_4)_{1-x}(\text{SeO}_4)_x$  with  $x = 0.50$  and  $1.00$ . Typical values of  $(1 - \Delta m/m_0)_{\text{obs}}$  for the same compositions are ca. 0.60 [0.412] and ca. 0.65 [0.389], respectively (calculated weight loss parameters in brackets).

Addition of selenate shifts the decomposition of  $(\text{IO})_2(\text{SO}_4)_{1-x}(\text{SeO}_4)_x$  to lower temperatures. The decrease as function of  $x$  is nearly linear and virtually the same for  $t_{\text{S},1}$ ,  $t_{\text{I},1}$  and  $t_{\text{E},1}$ , and amounts to ca.  $50^\circ\text{C}$  over the composition span between  $x = 0.00$  and  $1.00$ .

## References

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