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Dizirconium Trioxide Sulfate——$Zr_2O_3SO_4$

G. V. JERE,* V. RAMAN, and M. T. SANTHAMMA
Department of Chemistry, Indian Institute of Technology, New Delhi 110029, India

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Synopsis. Dizirconium trioxide sulfate $Zr_2O_3SO_4$ has been isolated and characterised. It is obtained as a thermally degraded product of peroxosulfatozirconium(IV) complex, $Zr_2(O_2)_3SO_4 \cdot 8$—$10H_2O$, around 400—500 °C. It contains zirconium, oxide oxygen and sulfate in its lattice.

The TGA curve[1)] of peroxosulfatozirconium(IV) complex, $Zr_2(O_2)_3SO_4 \cdot 8$—$10H_2O$, shows a relatively flat plateau in the region 350—600 °C. This indicates the formation of a stable intermediate compound. The present note deals with isolation and characterisation of this intermediate compound.

Experimental

The peroxosulphatozirconium(IV) complex — $Zr_2(O_2)_3SO_4 \cdot 8$—$10H_2O$— was prepared by the method reported.[1,2)] The dried solid was heated in a muffle furnace at *ca.* 450 °C for an hour in order to obtain the stable intermediate product. Several samples were prepared and analyzed for zirconium and sulfate contents. The difference in percentage, after subtracting the total value for zirconium and sulfate was assigned to the oxide oxygen. The analytical results are given below:

Composition (%)			Molar ratio		
Zr	SO_4^{2-}	O^{2-}	Zr :	SO_4^{2-} :	O^{2-}
55.92	28.60	15.48	1	0.49	1.58
56.69	28.78	14.53	1	0.48	1.46
56.44	29.02	14.54	1	0.49	1.47
Average composition					
56.35	28.80	14.85	1	0.49	1.50

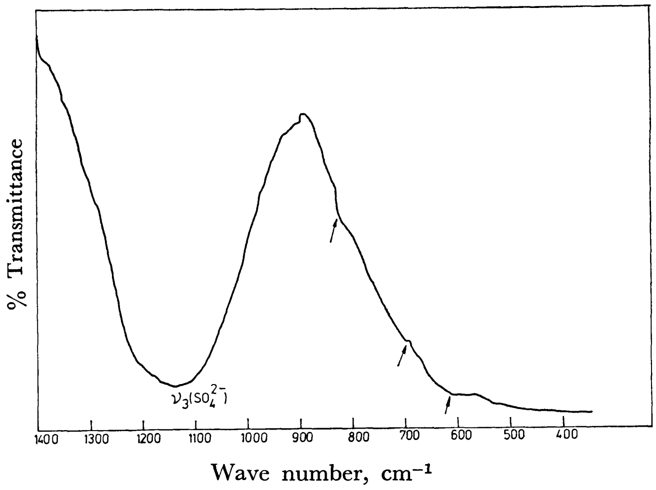

Fig 1. Salient features of the IR spectrum of $Zr_2O_3SO_4$.

The IR spectra of the samples were recorded in Nujol mull, on a Perkin Elmer double beam IR spectrophotometer, model 225. Salient features of the spectrum are given in Fig.1. TGA was carried out on a Stanton recording thermobalance, HT-D, with a 6 °C/min heating rate.

Discussion

We see that the molar composition of the species approximates Zr : SO_4^{2-} : O^{2-} as 1 : 0.5 : 1.5. The compound is formulated as $Zr_2O_3SO_4$. The formation of this compound as a thermally degraded product of the parent peroxo complex can be visualized as follows:

$$\underset{\text{(peroxo compound)}}{Zr_2(O_2)_3SO_4 \cdot 8\text{—}10\,H_2O} \xrightarrow[\text{(loss of water + peroxo oxygen)}]{400\text{—}450\,^\circ C} \underset{\text{(oxide sulfate)}}{Zr_2O_3SO_4}$$

This was indicated earlier also by Tikhomirov *et al.*[2)] The molar ratio zirconium to sulphate (1 : 0.5)remains the same both in the intermediate and its parent peroxo compound. It is seen from TGA study that the decomposition of sulfate group from the oxide sulfate commences at *ca.* 600 °C, showing that the sulfate is intact in it. In the IR spectrum of the compound (Fig.1), the ν_3 (SO_4) and ν_4 (SO_4) appear as strong and broad absorptions in the region 1200—1000 cm^{-1} and around 600 cm^{-1} respectively. These two degenerate modes show no splitting. ν_1 and ν_2 do not appear in the IR spectrum. This indicates that sulfate is ionic in nature[3)] in the oxide sulfate, unlike the case of the parent peroxo compound where it is of coordinated and bridging type.[1)] The sulfate group might have undergone some internal rearrangement during the thermal decomposition of the parent peroxo compound. It is seen that $Zr_2O_3SO_4$ characterised for the first time is an oxide sulfate of zirconium containing zirconium, oxide oxygen and sulfate in its lattice.

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References

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