

Iodine Oxides

Part IV. Solid Compounds
Formed in the Systems
 $\text{H}_2\text{O}-\text{SO}_3-\text{I}_2\text{O}_n$ ($n=3, 4, \text{ and } 5$)

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Compounds generated by reactions between sulphur trioxide and oxides of iodine were observed by Millon¹ as early as in 1844. Since that time, such compounds have been referred to in the literature at frequent intervals,²⁻²⁶ thus continually renewing a debate which includes such fundamental topics as their compositions, and chemical and physical properties.

A brief historical survey of these developments, up to 1963, was presented in the first of these articles.²² In recent years, Gillespie and coworkers²³⁻²⁶ have made significant contributions as a result of studies of the properties of the relevant compounds dissolved in sulphuric acid. Meanwhile, the work at this Institute on the solid

compounds of the ternary systems $\text{H}_2\text{O}-\text{SO}_3-\text{I}_2\text{O}_n$ ($n=3, 4, \text{ and } 5$) which are stable at ordinary temperatures has also been continued, and the object of this paper is to summarize our findings.

The substantial amount of information is conveniently presented in the form of the block diagram shown in Fig. 1. In the positive direction of the abscissa the SO_3 concentration increases, *i.e.* from H_2O through dilute H_2SO_4 in H_2O and concentrated H_2SO_4 to fuming $\text{H}_2\text{SO}_4-\text{SO}_3$ or pure SO_3 atmosphere, whereas the ordinate places the iodine oxides with the formal oxidation state of iodine increasing upwards. It should be emphasized that the scale of the abscissa is non-linear, but corresponds to a monotonically increasing SO_3 content. The diagram makes a distinction between the solid compounds which have been studied and confirmed in this research programme, and those which are quoted from the literature. The former category is indicated in Fig. 1 by means of larger type and a heavier line thickness than the latter. The same distinction applies to the paths of the syntheses which are shown by the lines connecting the blocks. The direction of the various synthetic paths is indicated by arrows. With

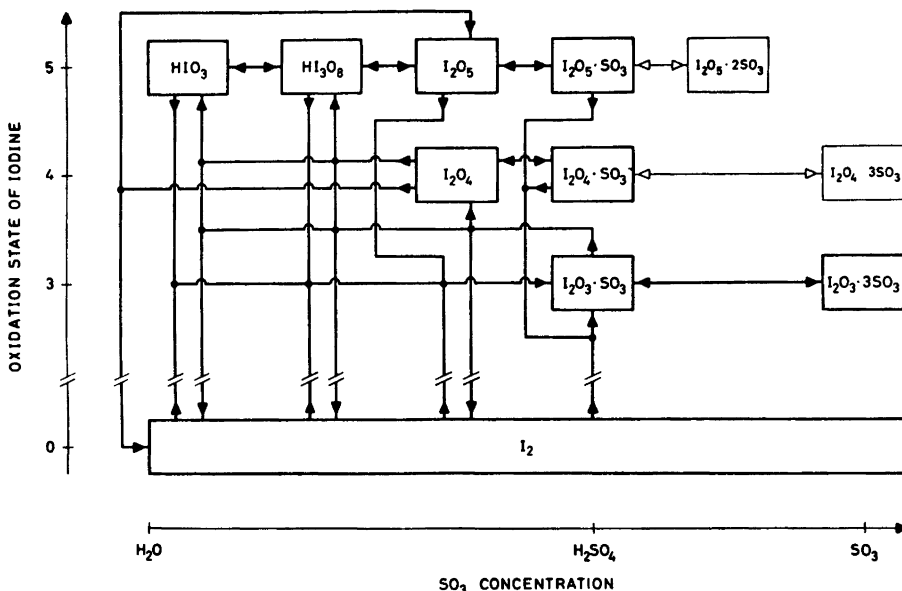


Fig. 1. Block diagram showing relationships between solid compounds of the systems $\text{H}_2\text{O}-\text{SO}_3-\text{I}_2\text{O}_n$ ($n=3, 4, \text{ and } 5$); all reactions at room temperature except $5\text{I}_2\text{O}_4=4\text{I}_2\text{O}_5+\text{I}_2$.

the exception of the irreversible decomposition of I_2O_4 into I_2O_5 and I_2 (which requires a temperature of 125 to 250°C in the absence of H_2O-SO_3), the other reactions all take place at room temperature.

Analogous to each of the compounds which include sulphur there appears to exist another containing selenium.^{19,22,27} In the synthesis of $I_2O_3 \cdot SO_3$ (and the analog $I_2O_3 \cdot SeO_3$) ICl or IBr may be substituted for I_2 .

The presentation here of equations for the overall reactions seems superfluous, and it is hoped that the diagram is sufficiently clear without further comment. A discussion of the detailed kinetics of the reactions which occur in solution will be the subject of a forthcoming paper. However, it seems appropriate to draw attention to the fact that the above mentioned irreversible decomposition of I_2O_4 to I_2O_5 and I_2 follows a quasi-reversible path through the intermediate compound $I_2O_3 \cdot SO_3$ (or $I_2O_3 \cdot SeO_3$). For this reason, considerable interest is attached to the structural arrangements of $I_2O_3 \cdot SO_3$ and $I_2O_3 \cdot SeO_3$. Determinations of the crystal structures of these compounds are therefore in progress at this Institute. The preliminary crystallographic data (from oscillation, Weissenberg, and Debye-Scherrer photographs) show that the two compounds belong to the orthorhombic system with the following approximate unit cell dimensions:

$$\begin{aligned} I_2O_3 \cdot SO_3: & \quad a = 15.24 \text{ \AA}, \quad b = 4.70 \text{ \AA}, \\ & \quad \quad \quad c = 8.00 \text{ \AA} \\ I_2O_3 \cdot SeO_3: & \quad a = 15.45 \text{ \AA}, \quad b = 4.78 \text{ \AA}, \\ & \quad \quad \quad c = 8.12 \text{ \AA} \end{aligned}$$

The cell content is four formula units. The systematic extinctions in the diffraction data are of the type hkl absent when $h+k=2n+1$ and $h0l$ absent when $l=2n+1$. The possible space groups are accordingly $Cmc2_1$, $C2cm$, and $Cmcm$. The two compounds are clearly isostructural, in accordance with an earlier suggestion of Dasent and Waddington.¹⁹ Data for characterization of these and other compounds included in Fig. 1 are to be found in the literature.^{18-22,28,29}

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