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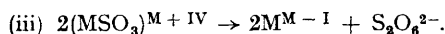
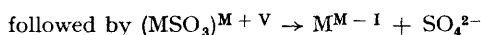
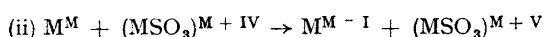
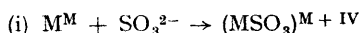
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## Oxidation of Non-metallic Substrates by Metal Complexes

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RECENTLY Vepřek-Šiška and his colleagues have investigated the products of oxidation of sulphite in aqueous solution by metal complexes which undergo 1-equivalent changes in their oxidation state.<sup>1</sup> They find that substitution-labile complexes give sulphite and dithionate, whereas substitution-inert complexes give sulphate only. Earlier discussions<sup>2</sup> of the mechanism of this oxidation implied that all 1-equivalent oxidants should yield some dithionate, formed through the dimerisation of free radicals,  $\cdot\text{SO}_3^-$ . Vepřek-Šiška has suggested the following mechanism in which free radicals do not participate:



Here  $\text{M}^{\text{M}}$  represents a complex metal-ion oxidant of oxidation state  $\text{M}$ , including its associated ligands, and  $\text{M}^{\text{M} - \text{I}}$  is a related reduced form. The formula  $(\text{MSO}_3)^{\text{M} + \text{IV}}$  represents an inner-sphere complex between sulphite and the oxidant, obtained by displacing one or more ligands from the metal ion by  $\text{SO}_3^{2-}$ ;  $(\text{MSO}_3)^{\text{M} + \text{V}}$  is formed from  $(\text{MSO}_3)^{\text{M} + \text{IV}}$  by the loss of one electron. Reactions (i), (ii), and (iii) occur with labile oxidants, but (i) and (ii) only with inert oxidants. Vepřek-Šiška explains this by postulating a difference between the species  $(\text{MSO}_3)^{\text{M} + \text{IV}}$  formed from labile as distinct from inert complexes. With labile complexes co-ordination between metal and sulphite is considered

to occur by metal-oxygen bonds, but with inert complexes by metal-sulphur bonds; this is said to prevent the sulphur-sulphur bond formation necessary in (iii).

We suggest an alternative interpretation of more general application. Owing to the slowness of substitution of substrate into an inert oxidising complex, the stationary-state concentration of  $(\text{MSO}_3)^{\text{M} + \text{IV}}$  is likely to be very low if, as we should expect, the rate constants for the following reactions are relatively large. Consequently, reaction (iii) is unlikely to occur, since its rate depends upon the square of the  $(\text{MSO}_3)^{\text{M} + \text{IV}}$  concentration and it involves the rupture of two inert metal-ligand bonds. In the formally parallel oxidation of hydrazine, where co-ordination isomerism of the type invoked with sulphite seems unlikely, there is already some evidence of a similar distinction between labile and inert oxidants. For example, the substitution-labile complex trispyrophosphatomanganate(III) oxidises hydrazine partly *via*  $\text{N}_4\text{H}_6$  (corresponding to  $\text{S}_2\text{O}_6^{2-}$ ) to  $\text{N}_2$  plus  $2\text{NH}_3$ , and partly *via*  $\text{N}_2\text{H}_2$  (corresponding to  $\text{SO}_4^{2-}$ ) to  $\text{N}_2$ .<sup>3</sup> With substitution-inert ferricyanide, no  $\text{NH}_3$  is produced.<sup>4</sup> We are presently investigating the oxidation of hydrazine with various complex ions to extend the comparison with the sulphite system and clarify the reaction mechanism. We find that the distinction foreshadowed above between inert and labile 1-equivalent oxidants in the hydrazine system is similar to that with sulphite.

The importance of the type of mechanism advanced by Vepřek-Šiška is that it provides an

alternative pathway for the oxidation of non-metallic substrates to routes involving free radicals when such routes are energetically unfavourable. Although for the reaction  $\text{Fe}^{3+} + \text{SO}_3^{2-} \rightarrow \text{Fe}^{2+} + \cdot\text{SO}_3^-$ ,  $\Delta G^\circ$  is *ca.* 10 kcal. mole<sup>-1</sup>, various aspects of the oxidation of sulphite by ferric ion, including the catalysis by cupric ion,<sup>2</sup> indicate the formation of free-radical intermediates, although this view has been contested.<sup>1b</sup> However, with weaker oxidants, *i.e.*, those of lower standard reduction potential, including many of those studied by Vepřek-Šiška, the free-radical route seems energetically improbable,  $\Delta G^\circ$  considerably exceeding 10 kcal.mole<sup>-1</sup> for the formation of  $\cdot\text{SO}_3^-$ . Here the preferable pathway is that in which the radical is not formed

in the free state, but is stabilised by complexing with the metal. With a sufficiently strong substitution-inert oxidant such as hexachloriridate(IV),  $E^\circ = 1.02$  v, the oxidation of sulphite or hydrazine by an outer-sphere reaction leading to free-radical formation is energetically feasible and we are presently investigating these reactions. Preliminary indications are that outer-sphere oxidations do occur and that little or no dithionate is produced in the oxidation of sulphite. We suspect, but have not yet established, that the latter is purely a kinetic effect and is due to oxidation of the free radicals by hexachloriridate(IV) before they encounter one another.

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<sup>1</sup> (a) J. Vepřek-Šiška and D. M. Wagnerová, *Coll. Czech. Chem. Comm.*, 1965, **30**, 1390; (b) J. Vepřek-Šiška, D. M. Wagnerová, and K. Eckschlager, *Coll. Czech. Chem. Comm.*, 1966, **31**, 1248; (c) J. Vepřek-Šiška, A. Šolcová, and D. M. Wagnerová, *Coll. Czech. Chem. Comm.*, 1966, **31**, 3287.

<sup>2</sup> W. C. E. Higginson and J. W. Marshall, *J. Chem. Soc.*, 1957, 447.

<sup>3</sup> W. C. E. Higginson, *Chem. Soc., Special Publ.*, 1957, No. 10, 95.

<sup>4</sup> L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine", Wiley, New York, 1951, p. 161.