

Aspects of Catalysis. Part VI.¹ Oxidations of Sulphoxides and Dioxan by Dioxygen

By H. Bernard Henbest* and Jadwiga Trocha-Grimshaw, Department of Chemistry, Queen's University, Belfast BT9 5AG

Some sulphoxides are oxidised to sulphones when treated with dioxygen in aqueous propan-2-ol in the presence of soluble iridium or rhodium catalysts. A catalyst derived from rhodium acetate and lithium chloride effects a reaction between dioxan and dioxygen to give a mixture of the di- and mono-formates of ethane-1,2-diol.

EXPERIMENTS concerned with the preparation and properties of iridium-sulphoxide complexes^{2,3} occasionally gave small amounts of a low-melting substance found to be dimethyl sulphone.

The deliberate oxidation of dimethyl sulphoxide to the sulphone was studied by passing air through a heated solution of the sulphoxide containing a potential catalyst. Oxidation to sulphone occurred in propan-2-ol containing 10% water when chlorides of iridium or rhodium were added (initially) to the reaction mixture. (Chlorides of ruthenium, osmium, and palladium were ineffective.) Under these conditions the chlorides may be expected to be converted partly or wholly into metal-sulphoxide complexes.

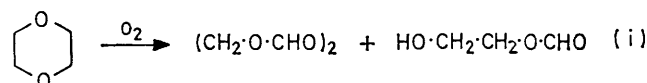
For iridium, the best catalyst (or catalyst source; see later) was the hydride $\text{IrHCl}_2(\text{Me}_2\text{SO})_3$.² When this complex was used, dimethyl sulphone was obtained in more than 90% yield after 15 h, the solution remaining clear yellow throughout the reaction. Oxidation proceeded only slowly during the first 3 h and then became more rapid, an indication that the hydride is transformed into a catalytically more active species. At the end of the reaction the iridium was recoverable as a gummy substance, the i.r. spectrum of which indicated the presence of metal-sulphoxide groups but which gave no evidence for the presence of IrH or IrO_2 groups. Attempted oxidation of dimethyl sulphoxide with the oxygen adduct, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2\text{O}_2$,⁴ as potential catalyst gave no sulphone. This does not exclude the intervention of iridium-peroxide complexes stabilised by sulphoxide ligands in the oxidation initiated by the hydride $\text{IrHCl}_2(\text{Me}_2\text{SO})_3$, for such complexes could be more reactive than the carbonyl phosphine compound (*cf.* the greater reactivity of hydrido-sulphoxide complexes than of other species²).

Rhodium(III) chloride and a related acid complex, $\text{H}[\text{RhCl}_4(\text{Me}_2\text{SO})_2]$, were similarly effective as catalysts (or sources) for the oxidation of dimethyl sulphoxide to sulphone. The acid complex was used to examine the oxidation of two other sulphoxides, which were in fact less readily oxidised. Although diphenyl sulphoxide gave a 65% yield of diphenyl sulphone in 22 h, a small amount of black material had precipitated; addition of hydrochloric acid (2 mol. equiv.) to the initial reaction solution prevented precipitation but the yield of sulphone

was lowered to 20%. Dibenzyl sulphoxide in 48 h gave 30% of the corresponding sulphone. It appears that the ease of oxidation falls with substituents in the order $\text{Me} > \text{Ph} > \text{PhCH}_2$.

Preliminary evidence indicated that sulphides are not readily oxidised under the conditions used for sulphoxides. This may be due to the formation of relatively stable sulphide complexes: for example, the compound $\text{RhCl}_3[(\text{CH}_2)_4\text{S}]_3$, was obtained when the oxidation of tetramethylene sulphide was attempted.

The investigation was extended to a study of the oxidation of dioxan: conversion into the di- and mono-formates of ethane-1,2-diol occurred in the presence of soluble rhodium species [equation (i)]. These two



products are among those formed in the aerial oxidation of dioxan being irradiated by ^{60}Co .⁵

Our initial findings were based on the use of rhodium(III) chloride. This dissolved in slightly aqueous dioxan to give a red solution, but oxidation (by oxygen passing through) was slow until the colour of the solution had changed to green (*ca.* 3 days). The dioxan was then fairly rapidly converted into the above two products. Addition of lithium chloride inhibited oxidation, and so it appeared that the formation of the more active catalyst present in the green solution required the replacement of one or more halide ligands, *e.g.* by carboxylate, originating from slow initial oxidation of dioxan. Rhodium carboxylates, $\text{Rh}_2(\text{OCOR})_4$, are green.

Rhodium acetate, $\text{Rh}_2(\text{OAc})_4$, was made⁶ and tested as a catalyst (source), but it was not particularly active owing to conversion into a yellow insoluble substance. Such precipitation was avoided by (a) using dry dioxan and (b) adding a little lithium chloride. Oxidation to the above two esters then proceeded steadily to completion within 2 days, the solution being clear green throughout. Both chloride and carboxylate groups are required to give an active catalyst.

EXPERIMENTAL

Oxidation of Sulphoxides with the Hydride Complex $\text{IrHCl}_2(\text{Me}_2\text{SO})_3$.²—A solution of dimethyl sulphoxide (142 mg) and the hydride (50 mg) in propan-2-ol (10 ml) and water (1 ml) was kept near its b.p. (reflux condenser) for

⁴ L. Vaska, *Science*, 1963, **140**, 809.

⁵ M. Galin-Vacherot, *Bull. Soc. chim. France*, 1963, [3], 765.

⁶ S. A. Johnson, H. R. Hunt, and H. M. Neuman, *Inorg. Chem.*, 1963, **2**, 960.

¹ Part V, H. B. Henbest and A. Zurqiyah, preceding paper.

² Part II, Y. M. Y. Haddad, H. B. Henbest, and J. Trocha-Grimshaw, *J.C.S. Perkin I*, 1974, 592.

³ Part III, Y. M. Y. Haddad, H. B. Henbest, J. Husbands, T. R. B. Mitchell, and J. Trocha-Grimshaw, *J.C.S. Perkin I*, 1974, 596.

15 h with oxygen bubbling through the clear pale yellow solution (*ca.* 20 ml min⁻¹). The solvent was evaporated off under reduced pressure and the residue was dissolved in a little water and extracted 5 times with dichloromethane. The extract was dried (MgSO₄) and filtered through a little deactivated alumina to give dimethyl sulphone (122 mg), m.p. 106–109°, identified by its i.r. spectrum. Evaporation of the yellow aqueous phase gave a non-crystalline residue.

In other experiments the course of the oxidation was monitored by g.l.c. analysis [2 m column of 2-cyanoethylmethylsilicone (XE-60) on AW-DMCS Chromosorb Q at 120 °C]. After 15 h, under the above reaction conditions, the ratio of sulphoxide to sulphone was *ca.* 5 : 95. The experiment was repeated (a) with sodium hydroxide (2 mol. equiv.) present (a brown reaction solution resulted and the yield of sulphone was reduced to 5%), and (b) with hydrochloric acid (2 mol. equiv.) [the yield of sulphone was reduced to 25% and another, unidentified product was formed (g.l.c. evidence)].

Use of the Rhodium Acid, H(Me₂SO)₂[RhCl₄(Me₂SO)₂].—The acid was prepared by dissolving rhodium(III) chloride hydrate (590 mg) in concentrated hydrochloric acid (0.7 ml) at 70°, followed by cooling to 20°, and addition of dimethyl sulphoxide (2 ml). The colour of the solution changed to lighter red, and crystals began to separate within 10 min. After 1 h the product (775 mg) was collected and washed with a little propan-2-ol to give the *acid* as red needles, m.p. 120–121° (Found: C, 17.0; H, 4.5; Cl, 25.5; S, 23.0. C₈H₂₅Cl₄O₄RhS₄ requires C, 17.2; H, 4.5; Cl, 25.4; S, 22.95%). Like the related iridium acids² it crystallises with two molecules of dimethyl sulphoxide of solvation.

(a) Dimethyl sulphoxide (142 mg) was oxidised in the presence of rhodium acid (56 mg) by the procedure used with the iridium complex. The solution was orange during the reaction, and a 70% yield of sulphone was formed (g.l.c. analysis) in 10 h. A similar result (80% sulphone) was obtained with rhodium(III) chloride (50 mg) and an oxidation time of 15 h. The sulphoxide was not oxidised when this last experiment was repeated with water (10 ml) alone as reaction solvent.

(b) A solution of diphenyl sulphoxide (234 mg) and rhodium acid (56 mg) in propan-2-ol (10 ml) and water (1 ml) was heated with oxygen bubbling through for 22 h. Some black material precipitated. Chromatography of the less volatile organic components over deactivated alumina (10 g) gave (elution with ether–light petroleum, 2 : 1) diphenyl sulphone (165 mg, 65%), m.p. 127–129°, identified by its i.r. spectrum, followed by (elution with ether) diphenyl sulphoxide (70 mg, 35%), m.p. 70° (i.r. spectrum).

When the reaction was carried out with hydrochloric acid (2 mol. equiv.) present the solution remained clear yellow. A 20% yield of diphenyl sulphone was obtained, together with much unchanged sulphoxide.

(c) Experiment (b) (initial conditions) was repeated with dibenzyl sulphoxide (315 mg). Chromatography over deactivated alumina (10 g) gave (elution with ether–light petroleum, 2 : 1) dibenzyl sulphoxide (185 mg, 70%), m.p. 132–134° (i.r. spectrum), followed by (elution with dichloromethane) dibenzyl sulphone (104 mg, 30%), m.p. 150–151° (i.r. spectrum).

(d) Procedure (b) was used with tetramethylene sulphide (300 mg). G.l.c. analysis showed that no appreciable amount of sulphoxide or sulphone had been formed. An

orange precipitate (30 mg), m.p. 188–189° separated during the reaction. This was the complex, RhCl₃[(CH₂)₄S]₃, which was also obtained by dissolving the acid H(Me₂SO)₂–[RhCl₄(Me₂SO)₂] (50 mg) in tetramethylene sulphide (0.1 ml) at 20 °C. After 30 min the orange precipitate was collected, dissolved in dichloromethane, and filtered through a small amount of deactivated alumina. The complex (12 mg) had m.p. 188–192° (Found: C, 31.0; H, 4.95; Cl, 22.2. C₁₂H₂₄Cl₃RhS₃ requires C, 30.4; H, 5.1; Cl, 22.45%).

Oxidation of Dioxan.—With rhodium(III) chloride. Rhodium chloride hydrate (26 mg) was added to purified dioxan (15 ml) containing 2% of water. The red solution was heated on a water-bath with a slow stream of oxygen passing through (20 ml min⁻¹). After 2–3 days the colour of the solution had changed to emerald green and the rate of formation of oxidation products increased. After a total of 4 days the reaction was largely complete. Fractional distillation gave a mixture (9.5 g) of the two main products (the mono- and di-formates of ethanediol), b.p. 40° at 17 mmHg, and then a fraction (2.4 g), b.p. 64–76° at 3 mmHg. A sample of the main fraction was separated by preparative g.l.c. (at 120 °C over a column containing 2-cyanoethylmethylsilicone) into ethanediol diformate and ethanediol monoformate (ratio 60 : 40), identical (i.r. spectra and g.l.c. behaviour) with authentic samples.⁷

Notes: (a) Water is present in the reaction mixture to bring the otherwise insoluble rhodium chloride into solution. One sample of commercial rhodium chloride was not completely soluble; oxidation was then slower. (b) Air can be used in place of oxygen but the reaction is then slower. (c) When formic acid (4.6 mg) was added to the initial reaction mixture the time for almost complete reaction was reduced from 4 to 3 days. (d) Addition of lithium chloride (4.1 mg) to the initial mixture resulted in a slower reaction: the solution remained red-brown and only about half the dioxan had been oxidised after 5 days. (e) No appreciable oxidation of dioxan occurred (during 7 days) (i) in the absence of rhodium chloride, or (ii) in the presence of rhodium metal (50 mg, prepared by precipitation from an aqueous solution). (f) No appreciable oxidation of dioxan occurred (2 days) in the presence of either iridium tetrachloride (100 mg) or cobalt naphthenate (250 mg).

With rhodium acetate, Rh₂(OAc)₄, and lithium chloride. Dioxan (15 ml), containing rhodium acetate (50 mg) and lithium chloride (10 mg) in solution, was treated with oxygen as in the experiments with rhodium chloride. After 27 h about half of the dioxan had been oxidised and after 2 days the oxidation was essentially complete. The reaction solution was green during the 2 days. The yields of the di- and mono-formates of ethanediol were similar to those obtained using rhodium chloride.

In the absence of the lithium chloride some yellow solid began to separate after 2 days. Oxidation proceeded steadily during the 2 days but was not complete until after a further 2 days. When this reaction was repeated with 2% water in the dioxan the yellow solid began to separate after only 1 day. After 2 days the solution was colourless; after 5 days only a small proportion of the dioxan had been oxidised.

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⁷ A. Henninger, *Ber.*, 1874, 7, 263.