

Catalysis of the Aerial Oxidation of Sulphoxides to Sulphones by Rhodium and Iridium Derivatives in Solution in Aqueous Propan-2-ol

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WHEN air is passed through a solution of dimethyl sulphoxide in hot propan-2-ol-water (9:1) containing rhodium or iridium chloride,† dimethyl sulphone is formed in a reaction solution that remains clear for at least 40 hr. After 16 hr. the yield of dimethyl sulphone is about 80% starting with rhodium(III) chloride, and 7–10% starting from iridium-(III) or -(IV) chloride or from the acid,¹ $\text{H}[\text{Cl}_4\text{Ir}(\text{Me}_2\text{SO})_2] \cdot 2\text{Me}_2\text{SO}$, m.p. 165–170°. The two neutral compounds,¹ *cis*- and *trans*- $\text{Cl}_3\text{Ir}(\text{Me}_2\text{SO})_3$, are similarly active, but the most effective iridium compound examined so far is the hydride,² $\text{HCl}_2\text{Ir}(\text{Me}_2\text{SO})_3$: oxidation is *ca.* 50% complete after 9 hr. and a 72% yield of dimethyl sulphone can be isolated after 15 hr.

A new acid, $\text{H}[\text{Cl}_4\text{Rh}(\text{Me}_2\text{SO})_2] \cdot 2\text{Me}_2\text{SO}$, m.p. 120–121° [prepared at 20° from rhodium(III)

chloride, concentrated hydrochloric acid, and dimethyl sulphoxide] is more active than the corresponding iridium acid, and also more active than rhodium(III) chloride especially at shorter operational times: after 4 hr. the yields of sulphone from dimethyl sulphoxide are 50 and 25% respectively from the acid and the trichloride.

At the end of these experiments with dimethyl sulphoxide, the iridium or the rhodium is recovered as a non-crystalline, but still catalytically active, material.

Preliminary experiments indicate that aryl sulphoxides are less readily oxidised than dimethyl sulphoxide. However, a 30% yield of dibenzyl sulphone is obtained by aerial oxidation of the related sulphoxide for 48 hr. with the rhodium acid. Diphenyl sulphoxide is also oxidised but

† A 20:1 molar ratio of sulphoxide:metal compound was generally used in this study.

a black precipitate slowly separates. This can be avoided by initially adding a sufficient amount of hydrochloric acid: a 20% yield of diphenyl sulphone is then obtained after 22 hr.

Thioethers are not readily oxidised by this

method. They react with the metal species to give metal-thioether complexes.

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¹ Y. M. Y. Haddad, H. B. Henbest, Mrs. J. Husbands, and T. R. B. Mitchell, *Proc. Chem. Soc.*, 1964, 361.

² Mrs. J. Trocha-Grimshaw and H. B. Henbest, *Chem. Comm.*, 1967, 544.