

## Selective Oxidation of Two Dialkyl Sulphides catalysed by Ruthenium Complexes

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Di-n-butyl and diethyl sulphide both undergo selective oxidation to the corresponding sulphoxide and sulphone on treatment with oxygen in ethanol in the presence of ruthenium(III) chloride. Some ruthenium complexes also catalyse the oxidation of di-n-butyl sulphide in benzene, but the extent and selectivity of the oxidation are much less than in ethanol. A non-radical mechanism seems to be the main pathway in both solvents, but no evidence for the involvement of a dioxygen complex has been obtained, and it is concluded that a redox mechanism is involved.

THE heterogeneous oxidation of organic monosulphides by air or oxygen in the presence of metal oxides has been extensively investigated,<sup>1,2</sup> but the possibility of using a homogeneous metal complex to catalyse these reactions does not seem to have been explored in such detail.

<sup>1</sup> A. V. Mashkina and L. B. Avdeyeva, *Khim. seraorg. Soedinenii, sodershasch. Neft. Nefteprod., Akad. Nauk S.S.S.R. Bashkirsk. Filial*, 1964, **7**, 37; A. V. Mashkina, *Khim. seraorg. Soedinenii, sodershasch. Neft. Nefteprod.*, 1968, **8**, 125; A. V. Mashkina, L. B. Avdeyeva, and V. F. Anufrienko, *Kinetics and Catalysis (U.S.S.R.)*, 1969, **10**, 508; A. V. Mashkina and V. I. Marshneva, *ibid.*, 1968, **9**, 683; P. S. Makoveev and A. V. Mashkina, *ibid.*, 1968, **9**, 863; 1969, **10**, 465; N. I. Polovinkina, P. S. Makoveev, and A. V. Mashkina, *ibid.*, 1970, **11**, 828; A. V. Mashkina, P. S. Makoveev, and I. I. Polovinkina, *ibid.*, 1972, **13**, 106; A. V. Mashkina, P. S. Makoveev, and A. P. Zeif, *ibid.*, 1969, **10**, 673; E. M. Davydova and A. V. Mashkina, *ibid.*, 1971, **12**, 574; E. M. Davydova, Y. M. Shchekochikhin, and A. V. Mashkina, *ibid.*, 1969, **11**, 1259; L. B. Avdeyeva and A. V. Mashkina, *Petroleum Chem. (U.S.S.R.)*, 1969, **9**, 198; T. M. Kogan and A. V. Mashkina, *ibid.*, 1970, **10**, 59; A. V. Mashkina, P. S. Makoveev, and N. I. Polovinkina, *Reakts. spos. org. Soedinenii*, 1969, **6**, 24; P. S. Makoveev and A. V. Mashkina, *Neftekhimiya*, 1969, **9**, 302; G. M. Batalina and V. A. Proskuryakov, *J. Appl. Chem. (U.S.S.R.)*, 1965, **38**, 2030.

Chlorides and chloride oxides of molybdenum, tungsten, and vanadium have been reported to catalyse the oxidation by oxygen of diethyl sulphide to S-ethyl ethanethiosulphonate (EtSO<sub>2</sub>·SEt) under mild conditions (60 °C and 70 lbf in<sup>-2</sup>),<sup>3</sup> and there is a brief mention<sup>2</sup> that copper(II) chloride catalyses the oxidation by air of di-n-butyl sulphide to the corresponding sulphoxide at 120 °C and 700 lbf in<sup>-2</sup>. Henbest and Trocha-Grimshaw investigated the homogeneous oxidation of sulphoxides to sulphones by air, catalysed by rhodium and iridium complexes, and commented that sulphides were not readily oxidised under the conditions used for sulphoxides.<sup>4</sup> It is known that some transition metal compounds can oxidise sulphides stoichiometrically; for example gold(III) chloride reacts with some sulphides to

<sup>2</sup> A. V. Mashkina and L. B. Avdeyeva, *Neftekhimiya*, 1968, **8**, 414.

<sup>3</sup> F.P. 2,044,265/1971.

<sup>4</sup> J. Trocha-Grimshaw and H. B. Henbest, *Chem. Comm.*, 1968, 1035; H. B. Henbest and J. Trocha-Grimshaw, *J.C.S. Perkin I*, 1974, 607.

give gold(I) and the corresponding sulphoxides,<sup>5</sup> and copper(II) chloride reacts with dimethyl sulphide to give sulphide complexes of copper(I),<sup>6</sup> dimethyl sulphoxide presumably also being formed.

This paper describes our attempts to find a homogeneous transition metal catalyst for the oxidation by air of di-n-butyl sulphide to the corresponding sulphoxide and sulphone, our intention being to obtain a high yield of sulphone.

#### RESULTS AND DISCUSSION

*Oxidations in Ethanol.—Autoclave reactions.* We first compared a number of transition metal halides as catalysts of the oxidation of a dilute solution of di-n-butyl sulphide in ethanol in an autoclave, with a 44 : 1 sulphide : catalyst molar ratio, at 100 °C and 500 lbf in<sup>-2</sup> of air, for 12 h. Copper(II) chloride gave a 10% yield of di-n-butyl sulphoxide, and copper(II) bromide was considerably more active, giving a 21% yield of sulphoxide, which could be improved to 89% if the reaction was carried out for 60 h; after this time a 2% yield of di-n-butyl sulphone had also been formed. The most active catalyst was ruthenium(III) chloride trihydrate, which gave an 18% yield of sulphoxide and a 76% yield of sulphone after 12 h. As ruthenium(III) chloride was so much more active than the other halides investigated, our further efforts were concentrated on this and other complexes of ruthenium.

An important feature of this ruthenium(III) chloride catalysed oxidation is its high selectivity for oxidation at the sulphur atom. As well as the 18 and 76% yields of, respectively, sulphoxide and sulphone, 3% of the starting material was recovered, so that no more than 3% of the sulphide can have undergone unselective oxidation. This contrasts with the radical-induced oxidation of dialkyl sulphides, which gives a mixture of products, including disulphides and carbonyl-containing compounds, believed to arise from initial attack at an  $\alpha$ -carbon atom.<sup>7</sup> The i.r. spectrum of the product of the ruthenium(III) chloride catalysed oxidation had weak bands at 1 990 and 2 030 cm<sup>-1</sup> (in carbon tetrachloride solution), probably due to Ru-H and/or Ru-CO species, although the possible presence of such species does not imply its/their involvement in the catalytic oxidation. Hydride and carbonyl complexes are known to be formed by the reaction of phosphine complexes of group 8 metals, including ruthenium, with alcohols,<sup>8</sup> and sulphide complexes may well behave similarly. The mixture of ruthenium carbonyl chlorides formed by bubbling carbon monoxide through a solution of ruthenium trichloride in ethanol<sup>9</sup> was completely inactive for the oxidation of

di-n-butyl sulphide under our conditions, and the formation of carbonyl species may therefore be a pathway for the deactivation of the catalyst. The ruthenium(III) chloride catalysed oxidation of di-n-butyl sulphide was accompanied by the oxidation of a substantial amount (*ca.* 10%) of the ethanol to a product identified by g.l.c.–mass spectrometry as acetaldehyde diethyl acetal; this oxidation also occurred in the absence of the sulphide and is reminiscent of the oxidation of alcohols catalysed by palladium(II) and copper(II);<sup>10</sup> the stoichiometric oxidation of alcohols to aldehydes by ruthenium(III) is also known.<sup>11</sup>

In an attempt to speed up the ruthenium(III) chloride catalysed oxidation of di-n-butyl sulphide, an oxidation was carried out at 150 instead of 100 °C, other conditions being kept the same. At this higher temperature the oxidation was much less selective, the yields of sulphoxide, sulphone, and recovered sulphide being respectively 1, 33, and 10%; the product had strong i.r. absorption between 1 600 and 1 800 cm<sup>-1</sup>, indicating the presence of carbonyl-containing compounds.

*Atmospheric pressure reactions.* In the hope of obtaining some mechanistic information about the ruthenium(III) chloride catalysed oxidation of dialkyl sulphides we carried out some experiments at atmospheric pressure. To avoid complications arising from the uncertain and variable composition of 'ruthenium(III) chloride trihydrate'<sup>12</sup> we used the well characterised complex RuCl<sub>3</sub>(Et<sub>2</sub>S)<sub>3</sub>,<sup>13</sup> which was prepared in good yield by treatment of ruthenium(III) chloride trihydrate with a large excess of diethyl sulphide in ethanol. To avoid having to study the products of the simultaneous oxidation of two sulphides, diethyl sulphide, rather than di-n-butyl sulphide, was used in the atmospheric pressure oxidations, and to speed up the reactions oxygen was used instead of air. When oxygen was bubbled through a solution (*ca.* 20%) of diethyl sulphide in ethanol in the presence of [RuCl<sub>3</sub>(Et<sub>2</sub>S)<sub>3</sub>] (sulphide : complex 20 : 1) at 70 °C, diethyl sulphoxide, followed by diethyl sulphone, began to accumulate. The slower formation of sulphone than of sulphoxide suggests that the reaction involves two stages, the sulphone being formed from the sulphoxide. The effect of added water on the reaction was then investigated, as Henbest and Trocha-Grimshaw used propanol containing 10% of water for their rhodium and iridium complex catalysed oxidations of sulphoxides (although they did not state explicitly that water was necessary or desirable).<sup>4</sup> The ethanol used for all the oxidations so far was 'absolute ethanol,' which contained 0.27% of water (although in the high pressure oxidations the reaction solution was exposed to air during assembly of

<sup>5</sup> F. Herrmann, *Ber.*, 1905, **38**, 2813.

<sup>6</sup> F. C. Phillips, *J. Amer. Chem. Soc.*, 1901, **23**, 250; H. J. Worth and H. M. Haendler, *ibid.*, 1942, **64**, 1232.

<sup>7</sup> L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 1955, 1596; L. Bateman, J. I. Cunneen, and J. Ford, *ibid.*, 1956, 3056.

<sup>8</sup> J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1960, 931; 1961, 290.

<sup>9</sup> J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466; M. L. Berch and A. Davison, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3763.

<sup>10</sup> W. G. Lloyd, *J. Org. Chem.*, 1967, **32**, 2816.

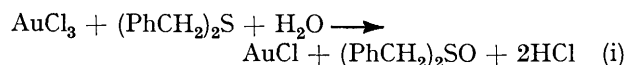
<sup>11</sup> R. K. Poddar and U. Agarwala, *Indian J. Chem.*, 1971, **9**, 477.

<sup>12</sup> W. P. Griffith, 'The Chemistry of the Rarer Platinum Metals,' Interscience, London, 1967, p. 136; G. Bremard, G. Nowogrocki, and G. Tridot, *Bull. Soc. chim. France*, 1974, 110.

<sup>13</sup> J. E. Fergusson, J. D. Karran, and S. Seevaratnam, *J. Chem. Soc.*, 1965, 2627.

the autoclave and therefore probably absorbed more water). Atmospheric pressure oxidations of diethyl sulphide were carried out with dried ethanol (0.01% water) and ethanol containing 10 and 30% of added water. The rates of formation of sulphoxide and sulphone during the first few hours of reaction did not vary significantly with the water content. During the later stages of the reaction the water content of all the solutions was no doubt increased because of the oxidation of ethanol to  $\text{MeCH}(\text{OEt})_2$ , so that interpretation of the results after longer reaction time is more difficult. However, it is remarkable that in all the solutions the rate of formation of sulphoxide and sulphone increased between 4 and  $22\frac{1}{2}$  h reaction time; this increase was most marked for the solution containing 30% of added water, so that the amounts of sulphoxide and sulphone were much greater in this solution after  $22\frac{1}{2}$  h than in the others. It is not surprising that the rate of formation of the sulphone, a secondary product, increased during the reaction, but the fact that the rate of formation of sulphoxide increased too suggests the possible formation of a more active catalyst than was present at the start of the reaction.

*Mechanistic studies.* The mechanism of the ruthenium-catalysed oxidation of diethyl or di-n-butyl sulphide is not obvious and, as just discussed, there may be more than one catalytic species, and therefore more than one mechanism, involved. With regard to the early stages of the reaction, it is possible that an intermediate complex containing co-ordinated oxygen<sup>14</sup> is involved, but we have found no evidence for any such complex, and we think it more likely, for reasons discussed below, that a redox mechanism, involving oxidation by ruthenium(III), followed by re-oxidation of a lower valent state of ruthenium [probably ruthenium(II)] by oxygen, is involved. The first stage of this mechanism has an analogy in the oxidation of dibenzyl sulphide by gold(III) [equation (i)].<sup>5</sup> Although



water is involved in a redox mechanism, the fact that the initial rate of oxidation of diethyl sulphide did not vary significantly with the concentration of water in the atmospheric pressure oxidations is understandable if water is not involved in the rate-determining step.

If the oxidation of sulphides does involve a redox mechanism, then ruthenium(III) should oxidise sulphides stoichiometrically in the absence of oxygen by a reaction similar to equation (i). The analogous reaction of ruthenium(III) with triphenylphosphine has been shown to give ruthenium(II), isolated as the complex  $[\text{RuCl}_2(\text{PPh}_3)_3]$ ; <sup>15</sup> triphenylphosphine oxide was presumably

† Wilkinson and his co-workers reported the analogous reaction of dimethyl sulphoxide with ruthenium(III) chloride to form  $[\text{RuCl}_2(\text{Me}_2\text{SO})_3]$ ,<sup>17</sup> but they were later unable to repeat this preparation;<sup>18</sup> in our hands  $\text{RuCl}_2(\text{Me}_2\text{SO})_4$  was formed under the same conditions as we had used for the preparation of  $[\text{RuCl}_2(\text{Bu}^n_2\text{SO})_3]$  from di-n-butyl sulphoxide and ruthenium(II) chloride.

the co-product, although as none was detected one cannot rule out the possibility that the ruthenium(III) was actually reduced by the methanol used as solvent, in which case formaldehyde would have been the co-product. Ruthenium(III) chloride reacted with an excess of di-n-butyl sulphide in refluxing ethanol under nitrogen to give a low yield [based on the amount of ruthenium] of di-n-butyl sulphoxide. The low yield suggested that the oxidation of di-n-butyl sulphide by ruthenium(III) is an equilibrium reaction as shown in equation (ii). In confirmation of this, a solution of



ruthenium(II) chloride in methanol, prepared by reduction of ruthenium(III) chloride with hydrogen,<sup>16</sup> reacted with an excess of di-n-butyl sulphoxide to form di-n-butyl sulphide and ruthenium(III), isolated as the sulphoxide complex  $[\text{RuCl}_3(\text{Bu}^n_2\text{SO})_3]$ .† The yield of di-n-butyl sulphide was greater than 100%, calculated on the basis of the amount of ruthenium used, in terms of the stoichiometry of equation (ii), and some di-n-butyl sulphide may have been formed by a ruthenium catalysed reduction of di-n-butyl sulphoxide by methanol. The oxidising power of dimethyl sulphoxide is known<sup>19</sup> and di-n-butyl sulphoxide appears to be a stronger oxidising agent than dimethyl sulphoxide from its reaction with ruthenium(II). The formation of ruthenium(III) suggests that at least some of the di-n-butyl sulphoxide was reduced by ruthenium(II), although it has been suggested that 'ruthenium(II) chloride' in fact contains a mixture of ruthenium(II) and ruthenium(III).<sup>20</sup>

With regard to the second stage of the oxidation, from di-n-butyl sulphoxide to the sulphone, a mechanism exactly analogous to equation (ii) seems reasonable. As before, this would require ruthenium(III) to react with di-n-butyl sulphoxide in the absence of air. Ruthenium(III) chloride in fact reacted with di-n-butyl sulphoxide to form the ruthenium(III) complex  $[\text{RuCl}_3(\text{Bu}^n_2\text{SO})_3]$ . However, with dimethyl sulphoxide the ruthenium(II) complex  $[\text{RuCl}_2(\text{Me}_2\text{SO})_4]$ <sup>18</sup> was formed; ruthenium(III) can, therefore, be reduced by sulphoxides.

The oxidation of ruthenium(II) to ruthenium(III) by oxygen is known to occur readily,<sup>16</sup> so that the stoichiometric oxidations of sulphide and sulphoxide proposed above could become catalytic in the presence of air or oxygen. The oxidation of di-n-butyl sulphide catalysed by other metal chlorides, e.g.  $\text{CuCl}_2$ , could also be explained by a redox mechanism. Presumably ruthenium is the most active metal because of a combin-

<sup>14</sup> V. J. Choy and C. J. O'Connor, *Co-ordination Chem. Rev.*, 1972, **9**, 145; J. S. Valentine, *Chem. Rev.*, 1973, **73**, 235.

<sup>15</sup> T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

<sup>16</sup> D. Rose and G. Wilkinson, *J. Chem. Soc. (A)*, 1970, 1791.

<sup>17</sup> J. D. Gilbert, D. Rose, and G. Wilkinson, *J. Chem. Soc. (A)*, 1970, 2765.

<sup>18</sup> I. P. Evans, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 204.

<sup>19</sup> W. W. Epstein and F. W. Sweat, *Chem. Rev.*, 1967, **67**, 247.

<sup>20</sup> E. E. Mercer and P. E. Dumas, *Inorg. Chem.*, 1971, **10**, 2755.

ation of favourable factors, *i.e.* (a) ruthenium(III) is able to oxidise sulphides to sulphoxides and sulphoxides to sulphones, (b) ruthenium(II) is readily re-oxidised by oxygen to ruthenium(III), and (c) the complexes formed between ruthenium(II) and/or ruthenium(III) and sulphoxides and/or sulphones are sufficiently labile to allow further oxidation to occur. If the simple complexes formed between ruthenium(III) and dialkyl sulphides, *e.g.*  $[\text{RuCl}_3(\text{Et}_2\text{S})_3]$ , are not involved in the oxidation of sulphides, then a further condition is that these complexes must also be reasonably labile. Henbest and Trocha-Grimshaw attributed the failure of their rhodium and iridium complexes to catalyse the oxidation of sulphides to the formation of stable sulphide complexes;<sup>4</sup> in support of this suggestion, ruthenium bonds more weakly to sulphides than does rhodium or iridium.<sup>13</sup> It is remarkable, however, that a chloride of ruthenium [presumably ruthenium(III)] was ineffective as a catalyst for the oxidation by air of dimethyl sulphoxide in hot propanol.<sup>4</sup>

*Oxidations in Other Solvents.*—Attempts were made to carry out some atmospheric pressure oxidations of diethyl sulphide under the same conditions as used for the oxidations in ethanol, but with other solvents, namely benzene, benzene saturated with water, acetonitrile, and acetonitrile plus 5% added ethanol. In all cases no oxidation of the diethyl sulphide had occurred after 24 h. Some autoclave oxidations of di-n-butyl sulphide were then carried out in benzene with a range of complexes as potential catalysts, the general conditions being the same as for the earlier autoclave oxidations in ethanol. The results are shown in Table 1. The five

TABLE 1  
Oxidation of di-n-butyl sulphide in benzene

Catalyst	Yield of $\text{Bu}^n_2\text{SO}$ (mol %)	Yield of $\text{Bu}^n_2\text{SO}_2$ (mol %)	Yield of other products (unselective oxidation) (mol %)
$[\text{FeCl}_2(\text{PPh}_3)_3]$	0	0	0
$[\text{RhCl}(\text{PPh}_3)_3]$	0	0	0
$[\text{Pt}(\text{O}_2)(\text{PPh}_3)_2]$	0	0	0
$[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$	4	0	3
$[\text{Cu}(\text{acac})_2]$	8	0	7
$[\text{Ru}(\text{acac})_3]$	0	0	0
$[\text{RuCl}_2(\text{PPh}_3)_3]$	24	2	16
$[\text{RuBr}_2(\text{PPh}_3)_3]$	35	3	15
$[\text{RuCl}_2(\text{PPh}_3)_3]$ + quinol (50 mg)	26	2	0
$[\text{RuCl}_2\{\text{P}(\text{OPh})_3\}_4]$	0	0	0
$[\text{RuCl}_2(\text{PPh}_3)_3]$ + $\text{P}(\text{OPh})_3$ (1:1)	31	2	6
$[\text{RuCl}_2(\text{PPh}_3)_3]$ + $\text{P}(\text{OPh})_3$ (1:2)	37	3	7
$[\text{RuCl}_2(\text{PhCN})_3]$	17	1	6
$[\text{RuCl}_2(\text{SbPh}_3)_3]$	13	0	4
$[\text{RuCl}_3(\text{AsPh}_3)_2\text{MeOH}]$	5	1	1
$[\text{Ru}_3\text{O}(\text{OAc})_6(\text{PPh}_3)_3]$	16	1	7

complexes of metals other than ruthenium were very poor catalysts, and the activities of the ruthenium complexes varied considerably. Tris(acetylacetonato)-ruthenium, for example, was completely inactive, but the triphenylphosphine complex  $[\text{RuCl}_2(\text{PPh}_3)_3]$  gave a 24%

yield of di-n-butyl sulphoxide, and the corresponding bromide,  $[\text{RuBr}_2(\text{PPh}_3)_3]$ , gave an even better yield of sulphoxide (35%) although the yield of sulphone in both cases was disappointingly low (only 2 or 3%). As well as the low conversions, another drawback of these oxidations was that, when oxidation did occur, a considerable proportion of products was formed by unselective oxidation (*i.e.* other than on the sulphur atom), as shown in the last column of Table 1. It seemed possible that the metal complexes were acting as radical initiators, and to investigate this possibility an oxidation was carried out in the presence of the radical inhibitor quinol. This prevented the formation of the products of unselective oxidation, but did not lower the yield of sulphoxide or sulphone. It therefore seems that these products are formed by a non-radical mechanism; as in the case of the oxidation in ethanol a redox mechanism seems the most likely, but the possibility of a dioxygen complex being involved cannot be excluded. Cenini *et al.* found that  $[\text{RuCl}_2(\text{PPh}_3)_3]$  catalyses the oxidation of triphenylphosphine to its oxide in benzene and postulated the intermediacy of a dioxygen complex,<sup>21</sup> but were unable to isolate one. James, however, suggested that this reaction may involve a redox process.<sup>22</sup> It was not surprising that, during the oxidations of di-n-butyl sulphide with  $[\text{RuCl}_2(\text{PPh}_3)_3]$  and  $[\text{RuBr}_2(\text{PPh}_3)_3]$  as catalysts, the triphenylphosphine underwent oxidation to the phosphine oxide, detected by i.r. spectroscopy. Since the oxidation of the triphenylphosphine might have been causing the catalysts to lose their activity, an oxidation was carried out with  $[\text{RuCl}_2(\text{PPh}_3)_3]$  as catalyst, to which 1 or 2 equiv. of the less readily oxidisable ligand triphenyl phosphite had been added. A slight increase in activity was observed. However, when the triphenyl phosphite complex  $[\text{RuCl}_2\{\text{P}(\text{OPh})_3\}_4]$  was used no oxidation occurred, possibly because of the difficulty of dissociation of any of the phosphite ligands. A number of ruthenium complexes were also investigated but none was as active as the 1:2 mixture of  $[\text{RuCl}_2(\text{PPh}_3)_3]$  and triphenyl phosphite. Even with this catalyst the extent of oxidation of the di-n-butyl sulphide was still far less than when ruthenium(III) chloride was used as the catalyst in ethanol. It would seem, therefore, that the ethanol plays an important part in the ruthenium complex catalysed oxidation of dialkyl sulphides.

#### EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer. G.l.c. measurements were made with a Pye 104 chromatograph and a flame-ionisation detector. A glass column (5 ft  $\times$  0.25 in diam.) containing 20% SP 1000 on Chromosorb W was used. For the analysis of di-n-butyl sulphide and its oxidation products a standard, dimethyl sulphone, was added to each mixture after the reaction; the column temperature was 100 °C for 6 min, and was then increased at 20 °C min<sup>-1</sup> to 155 °C. For

<sup>21</sup> S. Cenini, A. Fusi, and G. Capparella, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3576.

<sup>22</sup> B. R. James, *Inorg. Chim. Acta, Rev.*, 1970, 73.

following the oxidation of diethyl sulphide a standard, di-n-butyl sulphone, was added before the start of each reaction and samples were taken at intervals; the column temperature was 70 °C for 5 min, and was then increased at 40 °C min<sup>-1</sup> to 155 °C. Quantitative analyses were obtained from integrated peak areas by comparison with those of solutions of known concentration.

Autoclave reactions were carried out with 95 ml of solution in a Baskerville and Lindsay glandless rotary stirred autoclave fitted with a glass liner. The autoclave took *ca.* 1 h to reach the working temperature, and times of reaction refer to times after this period. The autoclave was pressurised at room temperature to 500 lbf in<sup>-2</sup> of air and then sealed; the operating pressure was therefore higher (*ca.* 650 lbf in<sup>-2</sup> at 100 °C).

Dried ethanol (containing 0.01% water) was obtained from 'absolute ethanol' (containing 0.27% water) by distillation from magnesium ethoxide.<sup>23</sup>

The complexes [FeCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>],<sup>24</sup> [Pt(O<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>],<sup>25</sup> [RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>],<sup>15</sup> [RuBr<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>],<sup>21</sup> [RuCl<sub>2</sub>{P(OPh)<sub>3</sub>}<sub>4</sub>],<sup>26</sup> [RuCl<sub>2</sub>(PhCN)<sub>3</sub>],<sup>17</sup> [RuCl<sub>2</sub>(SbPh<sub>3</sub>)<sub>3</sub>],<sup>17</sup> [RuCl<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub>MeOH],<sup>21</sup> and [Ru<sub>3</sub>O(OAc)<sub>6</sub>(PPh<sub>3</sub>)<sub>3</sub>]<sup>27</sup> were prepared by previously reported methods. Other materials were obtained from commercial sources.

TABLE 2  
Oxidation of diethyl sulphide in ethanol

Time (h)	Run 1 Yield (mg)		Run 2 Yield (mg)		Run 3 Yield (mg)		Run 4 Yield (mg)	
	Et <sub>2</sub> SO	Et <sub>2</sub> SO <sub>2</sub>	Et <sub>2</sub> SO	Et <sub>2</sub> SO <sub>2</sub>	Et <sub>2</sub> SO	Et <sub>2</sub> SO <sub>2</sub>	Et <sub>2</sub> SO	Et <sub>2</sub> SO <sub>2</sub>
1	2.9	0.5	3.7	0.7	2.7	0.2	3.0	0.1
2	8.0	1.5	10	1.1	4.6	0.3	8.0	0.1
4	14	2.5	23	1.0	9.0	0.3	19	0.3
6	23	4.1	29	2.0	17	0.5	52	1.3
22.5	162	26	206	19	244	40	646	92

**Autoclave Catalytic Reactions in Ethanol.**—In each case a solution of di-n-butyl sulphide (2.36 g, 16.1 mmol) and a transition metal halide (0.366 mmol) in ethanol (95 ml) under 500 lbf in<sup>-2</sup> of air was maintained at 100 °C for 12 h. Except where stated no di-n-butyl sulphone was formed. The molar yield of di-n-butyl sulphoxide (based on the amount of di-n-butyl sulphide used) was 4% with no halide present and ≤4% with the halides CrCl<sub>3</sub>·6H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, RhCl<sub>3</sub>·3H<sub>2</sub>O, PdCl<sub>2</sub>, and PtCl<sub>2</sub>. The percentage molar yield of sulphoxide with the following halides is shown in brackets after each: NaAuCl<sub>4</sub>·2H<sub>2</sub>O (6), FeCl<sub>2</sub>·4H<sub>2</sub>O (7), IrCl<sub>3</sub>·3H<sub>2</sub>O (9), CuCl<sub>2</sub> (10), OsCl<sub>3</sub>·3H<sub>2</sub>O (15), CuBr<sub>2</sub> (21), CuBr<sub>2</sub> (after 60 h) (89; 2% yield of sulphone also formed), RuCl<sub>3</sub>·3H<sub>2</sub>O (18; 76% yield of sulphone also formed).

**Trichlorotris(diethyl sulphide)ruthenium(III).**<sup>13</sup>—A solution of ruthenium trichloride trihydrate (5.00 g, 19.1 mmol) and diethyl sulphide (83.5 g, 926 mmol) in ethanol (600 ml) was refluxed for 1 h, then evaporated to low volume (*ca.* 50 ml). The red complex was filtered off, washed with cold ethanol, and dried (yield 6.67 g, 14.0 mmol, 73%) (Found: C, 30.0; H, 6.1; Cl, 22.2. Calc. for C<sub>12</sub>H<sub>3</sub>Cl<sub>3</sub>O<sub>3</sub>S<sub>3</sub>Ru: C, 30.2; H, 6.3; Cl, 22.3%).

**Atmospheric Pressure Catalytic Reactions.**—In each case a solution of the complex [RuCl<sub>3</sub>(Et<sub>2</sub>S)<sub>3</sub>] (0.50 g, 0.105 mmol),

diethyl sulphide (1.88 g, 20.8 mmol), and di-n-butyl sulphone [g.l.c. standard (100 mg)] in the solvent (10 ml) was maintained at 70 °C under a cold condenser, and a slow stream of oxygen was bubbled through. The results of the experiments with ethanol containing 0.01% (run 1), 0.27% (run 2), 10% (run 3), and 30% (run 4) of water are shown in Table 2.

**Non-catalytic Reactions.**—These were all carried out under dry nitrogen.

**Ruthenium(III) chloride and di-n-butyl sulphide.** A solution of ruthenium(III) chloride trihydrate (1.25 g, 4.78 mmol) and di-n-butyl sulphide (2.40 g, 16.4 mmol) in ethanol (50 ml) was refluxed for 6 h. G.l.c. then revealed the presence of di-n-butyl sulphoxide (0.12 g, 0.74 mmol).

**Ruthenium(II) chloride and di-n-butyl sulphoxide.** A solution of ruthenium(III) chloride trihydrate (981 mg, 3.75 mmol) in methanol (20 ml) was reduced to blue ruthenium(II) chloride.<sup>16</sup> The solution was filtered, degassed several times with nitrogen to remove all traces of hydrogen, and then added to a solution of di-n-butyl sulphoxide (3.22 g, 19.8 mmol) in methanol (10 ml). The solution was refluxed for 4 h. G.l.c. then showed the presence of di-n-butyl sulphide (534 mg, 3.65 mmol). The experiment was repeated with ruthenium trichloride trihydrate (460 mg,

1.76 mmol) and di-n-butyl sulphoxide (4.30 g, 26.5 mmol). After being refluxed for 3 h the solution was cooled to room temperature and evaporated to *ca.* 5 ml. Diethyl ether (*ca.* 10 ml) was added, and the precipitate of *trichlorotris(di-n-butyl sulphoxide)ruthenium(III)* was collected, washed with a little diethyl ether-methanol (2:1), and dried (yield 800 mg, 1.15 mmol, 65%) (Found: C, 43.2; H, 9.1; Cl, 15.1. C<sub>24</sub>H<sub>54</sub>Cl<sub>3</sub>O<sub>3</sub>S<sub>3</sub>Ru requires C, 41.5; H, 7.8; Cl, 15.3%);  $\nu_{\max}$  (Nujol) 1 077 and 1 107 cm<sup>-1</sup>.

**Ruthenium(III) chloride and di-n-butyl sulphoxide.** A solution of ruthenium(III) chloride trihydrate (198 mg, 0.757 mmol) and di-n-butyl sulphoxide (820 mg, 5.05 mmol) in methanol (15 ml) was refluxed for 4 h. Removal of the methanol by evaporation at room temperature gave a yellow oil to which was added pentane (10 ml). Yellow crystals of *trichlorotris(di-n-butyl sulphoxide)ruthenium(III)* were precipitated, collected, and dried (yield 460 mg, 0.663 mmol, 88%) (Found: C, 42.6; H, 8.4; Cl, 15.1. C<sub>24</sub>H<sub>54</sub>Cl<sub>3</sub>O<sub>3</sub>S<sub>3</sub>Ru requires C, 41.5; H, 7.8; Cl, 15.3%);  $\nu_{\max}$  (Nujol) 1 077 and 1 107 cm<sup>-1</sup>.

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