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THE HETEROGENEOUS CATALYTIC OXIDATION OF DIBENZOTHIOPHENE

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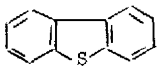
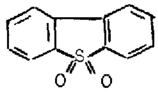
The catalytic oxidation by dioxygen of dibenzothiophene (1) has apparently not been reported, although thiophene and benzothiophene have recently been shown to undergo oxidation at 400°C in the presence of MoO_3-TiO_2 to respectively maleic anhydride and benzoic acid.[1] We report here the oxidation of (1) in high yield to dibenzothiophene-5, 5-dioxide (2) in the presence of a ruthenium catalyst.



(1)



(2)

On heating a solution of (1) in benzene (ca 0.1 M) in the presence of 5 per cent ruthenium on alumina ((1):Ru molar ratio = 11:1) at 100°C and 70 atm of air for 12 h, pure (2) was obtained in 97 per cent yield. Benzene was the preferred solvent for the catalytic oxidation of (1); in heptane the yield of (2) was much lower and in ethanol (1) could be recovered quantitatively. The catalyst used was a commercial sample, but it was later found that a catalyst could be prepared by treatment of alumina powder with a solution of a ruthenium compound (eg $RuCl_3$ in water, $Ru_3(CO)_{12}$ or $Ru(acac)_3$ in benzene), followed by removal of the solvent and reduction of the solid in a stream of hydrogen at 500°C. The activity of the catalyst depended on the ruthenium compound used in the sequence $Ru_3(CO)_{12} > Ru(acac)_3 > RuCl_3$. Ruthenium on carbon or silica was much less active than ruthenium on alumina.

Variation of the ratio of (1):Ru has shown that the activity of the ruthenium (defined as moles of (2) produced per mole of Ru) decreased as the molar ratio of (1):Ru is increased from 11:1 to 60:1. Furthermore, a catalyst that had been used to oxidise one batch of (1) was considerably less active when used for the oxidation of a second batch, and a catalyst could be completely deactivated by prolonged heating in air in the absence of (1). These results suggest that slow poisoning of the ruthenium accompanies the oxidation of (1). Experiments to regenerate the catalyst have not been carried out.

Dibenzothiophene-5-oxide was not detected in a mixture of (1) and (2) obtained by partial oxidation; however, in a separate experiment the 5-oxide was found to undergo catalytic oxidation faster than (1) and so it may be an intermediate in the conversion of (1) into (2).

Other metals supported on alumina have also been investigated as possible catalysts for the oxidation of (1), but none approached the activity of ruthenium. Platinum and iridium each gave a trace of (2), but palladium, rhodium, osmium and copper were completely inactive.

Di-n-butyl sulphide could also be oxidised in the presence of ruthenium on alumina. Under the conditions used for the oxidation of (1) but using instead di-n-butyl sulphide (ca 0.2 M, molar ratio of di-n-butyl sulphide:Ru = 21:1), di-n-butyl sulphoxide and sulphone were obtained in respectively 44 and 9 per cent molar yields, 46 per cent of the di-n-butyl sulphide being recovered. Although dialkyl sulphides have previously been shown to undergo catalytic oxidation in the presence of a number of metal oxides,[2] the combination of activity and selectivity of oxidation at the sulphur atom shown by ruthenium seems to be most exceptional.

REFERENCES

1. M. Blanchard and J. Goichon, Bull. Soc. Chim. France, 1975, 289.
2. A.V. Mashkina and L.B. Avdeyeva, Neftekhimiya, 1968, 8, 414.
   A.V. Mashkina, L.B. Avdeyeva and V.F. Anufrienko, Kinetics and Catalysis (USSR), 1969, 10, 508.