

Formation of Aldehyde in the Pyrolysis of Alkyl Sulphoxides

By D. G. BARNARD-SMITH and J. F. FORD

(The British Petroleum Company Limited, B.P. Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex)

IN a number of studies¹⁻⁴ of the pyrolysis of sulphoxides the formation of olefins as primary products has been reported. Evidence² has been presented to show that olefin formation occurs by an *Ei* decomposition of a cyclic intermediate formed by hydrogen-bonding between the β -hydrogen atom and the sulphoxide oxygen. In

the course of a detailed study of the influence of structure on the rates of pyrolysis of sulphoxides, particularly alkyl sulphoxides, we have discovered that the yields of olefin are often significantly lower than 100 mole/100 moles of sulphoxide decomposed and that the difference is mainly made up by aldehyde, which we believe is another primary

¹ L. Bateman, M. Cain, T. Colclough, and J. I. Cunneen, *J. Chem. Soc.*, 1962, 3570.

² C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, 1960, **82**, 1810.

³ C. Walling and L. Bollyky, *J. Org. Chem.*, 1964, **29**, 2699.

⁴ I. D. Entwistle and R. A. W. Johnstone, *Chem. Comm.*, 1965, 29.

product. For example, the decomposition of di-n-butyl sulphoxide (0.1—1.5M in cetane) at 180° (in sealed glass ampoules in the absence of air) showed first-order kinetics ($10^4 k_1 = 4.1 \text{ sec.}^{-1}$, $E_A = 32 \text{ kcal./mole}$) and gave the following products at 90 mole % decomposition: but-1-ene, (50), n-butyraldehyde, (36), di-n-butyl sulphide, (12), n-butyl s-butyl sulphide, (11), di-n-butyl disulphide, (37), water, (72). The figures in brackets refer to yields expressed as moles/100 moles of sulphoxide decomposed. With the exception of n-butyl s-butyl sulphide these yields were substantially independent of the extent of reaction. In experiments in which volatile products were removed continuously, the rate of decomposition was unchanged but the yield of n-butyl s-butyl sulphide was reduced, n-butane-1-thiol appeared in the products, and the yield of but-1-ene increased correspondingly.

⁵ E. Fromm and O. Achert, *Ber.*, 1903, **36**, 534.

⁶ R. Pummerer, *Ber.*, 1909, **42**, 2282.

⁷ E. E. Reid, "Organic Chemistry of Bivalent Sulphur", Volume III, Chemical Publishing Co., Inc., New York, 1960, p. 320.

The formation of aldehyde in the thermal decomposition of a sulphoxide has been previously noted only in the case of dibenzyl sulphoxide⁵ but is well known to occur in the decomposition of sulphoxides catalysed by strong acid, the Pummerer⁶ reaction. We suggest that the formation of n-butyraldehyde in the thermal decomposition of di-n-butyl sulphoxide occurs *via* the enol form of the sulphoxide which under the influence of heat rearranges to the corresponding hemithioacetal, *i.e.*, the hydroxyl group migrates from the sulphur atom to the α -carbon atom, probably *via* ionic intermediates. Hemithioacetals are well known⁷ to break down readily to give a thiol and aldehyde. In sealed-tube experiments the thiol is not observed and reaction of this with but-1-ene is the most probable source of the n-butyl s-butyl sulphide.

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