The Gas-phase Reactions of Sulphur with Diethylamine and Related Compounds

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SECONDARY amines are well-known as catalysts for sulphur oxidation reactions[1] and themselves undergo oxidation by sulphur at the nitrogen or a carbon atom to give a variety of products. For example, at 30°, sulphur and diethylamine yield *N*-trithiodiethylamine[2] and at 150°, *N*-ethylthioacetamide.[3] We are reporting on the gas-phase reaction of sulphur with diethylamine, ethylidene-ethylamine, and *N*-ethylthioacetamide at elevated temperatures.

The apparatus consisted of a pyrex glass or quartz reaction tube (vol. 500 ml.) mounted in a furnace. In the experiments reported, nitrogen (100 l./hr.) was saturated with sulphur vapour, by passage through molten sulphur at 325°, and blown into the reactor through a heated inlet tube. Similarly, a second nitrogen stream (100 l./hr.) was saturated with the reactant vapour. The reactant was cooled to 0° for diethylamine, $-8°$ for ethylidene-ethylamine and heated to 166° for *N*-ethylthioacetamide to give the required vapour pressure. The exit gases from the furnace

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[1] W. A. Pryor, "Mechanisms of Sulphur Reactions", McGraw Hill, 1962.
[2] T. G. Levi, *Gazzetta*, 1931, **61**, 286.
[3] C. L. Levesque, U.S. Patent No. 2,560,296.

were cooled to 100° in two traps where the unreacted sulphur and tar-like materials were condensed. A third trap removed most of the products condensable at −78°. Samples of the remaining gaseous products were collected in receivers of known volume. During the reaction, at 500°, hydrogen sulphide was produced and detected by bubbling the exit gases through cadmium acetate solution. Liquid and gas samples were analysed by gas chromatography. For identification, samples of the products were purified by preparative gas-chromatography.

The condensable products contained, in addition to the original reactant, acetonitrile and a third component, b.p. 129°, which was identified as 2-methylthiazole by its mass spectrum (a molecular ion at mass 99 and an isotopic ratio which indicated the presence of one sulphur atom per molecule), elemental analysis (C_4H_5NS) and infrared spectrum (identical with the reported spectrum for 2-methylthiazole[4]). Our results are summarized in the table.

Although sulphur vapour consists of S_8, S_6, S_4, and S_2 in appreciable quantities at 500°, the kinetics of the homogeneous reaction between methane and sulphur, from 550° to 625°, have been satisfactorily explained by the participation of the S_2 species only.[5] In many ways the reactions of S_2 are analogous to those of O_2, *e.g.*, dehydrogenation and oxidation of hydrocarbons occurs in the gas phase. The tabulated product yields indicate that the diethylamine is dehydrogenated to ethylidene-ethylamine rather than oxidised to *N*-ethylthioacetamide during the formation of acetonitrile and 2-methylthiazole. The reaction is therefore comparable to the dehydrocyclization reaction of n-butane with sulphur to give thiophen where butenes and butadiene are intermediates.[6]

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TABLE

Yields of Acetonitrile and 2-Methylthiazole
(Percentages are wt./wt. on reactant consumed)

Reactant	*Acetonitrile* (%)	*2-Methylthiazole* (%)
Diethylamine	7·1	37·2
Ethylidene-ethylamine	10·8	57·0
N-Ethylthioacetamide	5·4	0·2

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[4] A. Taurins, J. G. E. Fenyes, and R. N. Jones, *Canad. J. Chem.*, 1957, **35**, 423.
[5] R. A. Fisher and J. M. Smith, *Ind. Eng. Chem.*, 1950, **42**, 704.
[6] H. E. Rasmussen, R. C. Hansford, and A. N. Sachanen, *Ind. Eng. Chem.*, 1946, **38**, 376.