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STRUCTURE OF THE COMPOUND FROM TRIMETHYLAMINE OXIDE AND SULFUR DIOXIDE: AN AMINE OXIDE REARRANGEMENT

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Our general interest in demethylation studies of tertiary amine oxides (1) prompted us to re-examine the compound of proposed structure 1 from trimethylamine oxide and sulfur dioxide (2). The substance, m.p. 162-164°, was reported to form in a variety of solvents in over 90% yield and to undergo hydrolytic breakdown on refluxing with 5N - hydrochloric acid or 5N - sodium hydroxide to give ca. 75% of each of dimethylamine and formaldehyde and quantitative recovery of sulfur dioxide.

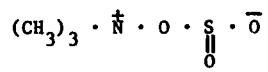
We obtained the same compound, m.p. 162°, from either anhydrous trimethylamine oxide or from the dihydrate in several solvents including liquid sulfur dioxide. However, our studies of the IR and NMR spectra of the substance do not support structure 1 and we propose an alternative structure 2.

The IR spectrum showed two bands at 2860 and 2785 cm^{-1} which could be assigned to $\overset{+}{N}H$ stretching (3). After treatment with D_2O these bands disappeared and were replaced by new bands at 2300 and 2240 cm^{-1} assignable to $\overset{+}{N}D$ stretching.

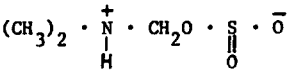
Further evidence for structure 2 was obtained from 60 MHz NMR data. In D_2O the NMR spectrum showed sharp singlets at δ 3.10 ($N-CH_2$, 6H) and 4.30 ppm ($N-CH_2$, 2H) which could not be explained by structure 1 but are in agreement with structure 2.

In liquid sulfur dioxide the NMR spectrum at -25° showed a total of 9 protons. A doublet (J = 5 Hz) at δ 2.47 ppm (6H) and a second doublet (J = 6 Hz) at 3.38 ppm (2H) were due, respectively, to the $N-CH_3$ and $N-CH_2$ protons split by the adjacent NH. The latter could be seen as a fairly sharp signal (1H) at 8.00 ppm at this temperature, but became very broad at +20°.

The compound was recovered unchanged from liquid sulfur dioxide.



1



2

The zwitterionic structure 2 is that of an internal salt of a sulfite monoester of the methylolamine rearrangement product of 1, and had been earlier (4) suggested as an intermediate in this reaction, and a mechanism for its formation proposed. The isolation of 2 represents the first instance in which the postulated methylolamine intermediate in the amine oxide rearrangement could in fact be isolated as a stable entity in a structure in which the nitrogen is not part of an amide moiety (5).

In our hands the breakdown of 2 was found to occur with surprising ease, e.g., at or below room temperature with dilute barium or sodium hydroxide, and dimethylamine, formaldehyde, and sulfur dioxide could each be readily isolated in the yields stated (2) and under much milder conditions than those earlier described (2).

The remarkably facile rearrangement of 1 → 2, and the application of the reaction to other amine oxides, are being further investigated.

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