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CXI.—*The Action of Sulphuric Acid on Paraformaldehyde.*

By JOHN GUNNING MOORE DUNLOP.

PRATESI (*Gazzetta*, 1885, **14**, 139) obtained α-trioxymethylene by heating paraformaldehyde in sealed tubes at 115° with small quantities of concentrated sulphuric acid. Kraut (*Annalen*, 1890, **285**, 95), and also Auerbach and Barschall (*Arbeit Kais. Gesund. Amt.*, 1907, **27**, 183), could not prepare α-trioxymethylene in this way, but did not study the reaction further.

On repeating Pratesi's work, using a bent tube, with the cool end immersed in cold water, a mobile liquid was obtained, but no α-trioxymethylene could be found. A considerable amount of carbon monoxide was also produced.

The same products were also obtained by heating paraformaldehyde (100 parts) with concentrated sulphuric acid (8 parts) in a straight tube for twenty-four to thirty-six hours at 115—120°, the mass being converted into a brown, or colourless, liquid, which was then fractionally distilled.

On distillation the liquid separated into methyl formate (20—22 parts), boiling at 33°, and a less volatile fraction (25—30 parts),

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which boiled at 90—100°. The residue in the distilling flask consisted of a black tar, from which some unchanged paraformaldehyde could be distilled. The use of a larger quantity of sulphuric acid led to charring, whilst if a smaller proportion was taken, part of the paraformaldehyde remained unchanged in the tube.

The fraction boiling at 90—100° had no fixed boiling point, had a strong odour of formaldehyde, and was soluble in water or alcohol, but sparingly so in benzene. Analyses and vapour-density determinations did not give concordant results, and yielded no clue to its components. On redistillation a little paraformaldehyde was deposited from the fractions of higher boiling point.

On saturating the liquid with hydrogen chloride, it separated into two layers, the lighter of which proved to be chloromethyl ether, $CH_3 \cdot O \cdot CH_2Cl$. It thus appeared that the liquid boiling at 90—100° closely resembled the product which Reychler obtained (*Bull. Soc. chim.*, 1907, [iv], **1**, 1189) on dissolving paraformaldehyde in methyl alcohol containing a trace of sodium methoxide. The addition of a little water to the material obtained by Reychler's method yielded a product apparently identical with the liquid boiling at 90—100° described above.

As Reychler has shown (*loc. cit.*) that the liquid product contains hydroxymethyl ether and somewhat indefinite compounds of the type $CH_3 \cdot O \cdot [CH_2 \cdot O]_n \cdot CH_2 \cdot OH$, produced by the condensation of methyl alcohol with paraformaldehyde, it would seem that methyl alcohol is produced during the action of sulphuric acid on paraformaldehyde. The absence of methyl alcohol and of its simple derivatives from the original paraformaldehyde was proved by saturating the latter with hydrogen chloride; no chloromethyl ether was formed. The methyl alcohol necessary for the production of the liquid boiling at 90—100° must therefore result from the decomposition of part of the methyl formate into the alcohol, carbon monoxide, and water, the methyl formate, in turn, being produced by the condensation of two molecules of formaldehyde.

The yield of methyl formate was fairly constant, and identical results were obtained with various samples of commercial paraformaldehyde. Attempts to obtain ethyl acetate in a similar manner from paracetaldehyde were unsuccessful.

When zinc chloride was substituted for the sulphuric acid, very great pressure was developed in the tube, and a large yield of methyl formate was obtained. In this case, however, none of the liquid of higher boiling point was formed.

Litterschied and Thimme (*Annalen*, 1904, **334**, 1) used trimethylamine to identify chloromethyl ether. The author, endeavouring to find a more convenient base for this purpose, treated

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dimethylaniline with chloromethyl ether. Colourless crystals were obtained, which melted at 227°. These proved, however, to be, not the expected quaternary salt, but the hydrochloride of tetramethyl-*p*-diaminodiphenylmethane, $CH_2(C_6H_4{\cdot}NMe_2)_2,2HCl$.

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