

### 73. *The Preparation of Liquid Monomeric Formaldehyde.*

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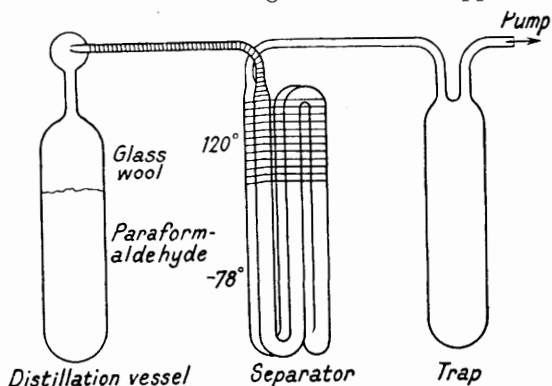
LIQUID formaldehyde was first prepared by Kekulé (*Ber.*, 1892, **25**, 2435) and later by Sachs (*Ber.*, 1899, **31**, 1231) by heating paraformaldehyde and condensing the distillate in liquid air. The product melted to an extremely unstable liquid, which polymerised readily to a solid cake of white polyoxymethylene with the evolution of heat. It was shown by Auerbach and Barschall (*Arb. Kais. Gesundh.*, 1907, **27**, 183), however, that paraformaldehyde contains only 94.2%  $\text{CH}_2\text{O}$ , the remainder being water. Later, Trautz and Ufer (*J. pr. Chem.*, 1926, **113**, 105) devised a method for the separation of the water, the condensate in the first trap being allowed to warm very slowly so that the liquid portion ran

to the bottom of the vessel, leaving behind a considerable fraction of polymerised solid, which contained the whole of the water. The liquid was redistilled into a second trap of special form, where a clear specimen finally collected at the bottom. Trautz and Ufer showed that the vapour obtained from the liquid obeyed the gas laws and was indeed monomeric formaldehyde. Their investigation of the polymerisation of the gas has recently been extended by Spence (J., 1933, 1193), who found, however, that Trautz and Ufer's method yielded liquids of varying stability: some remained mobile and transparent on warming to the boiling point, whilst others polymerised with extraordinary vigour. The liquid monomeric has also been obtained in a comparatively stable form by distillation of the alkali-precipitated polyoxymethylene (Walker, *J. Amer. Chem. Soc.*, 1933, 55, 2821).

Numerous experiments have indicated that the instability of previous preparations from paraformaldehyde might be ascribed (*a*) to the presence in the initially evolved gas of incompletely disintegrated portions of the paraformaldehyde chain, hydrated molecules, etc., which would probably act as centres of polymerisation if present in the liquid; and (*b*) to the presence of oxygen adsorbed on the walls of the containing vessels. The apparatus shown in the fig. eliminates these factors; during the past year, it has uniformly given samples of a high order of stability and having no tendency to polymerise explosively.

#### EXPERIMENTAL.

Paraformaldehyde was prepared by evaporation to dryness of a 40% solution of formaldehyde. The product was broken up, dried in a vacuum desiccator over sulphuric acid for 2 days, powdered, and placed in the distillation vessel (30 mm. diameter and 100 mm. long). A thick



wad of glass wool was introduced to prevent particles of the solid being carried over into the condensing system during the distillation, and the vessel was sealed to the apparatus as shown in the fig. The separator vessel consisted of a 10-mm. tube folded into three U-tubes in a compact block (20 cm. long), the upper part of which was wrapped with nichrome wire and asbestos. This, together with the tube leading to the distillation vessel, was maintained at 100–120°, and the lower, unwrapped portion immersed in carbon dioxide-ether. The system was first pumped out by a mercury-diffusion pump, and the condensing vessels heated with a Bunsen flame. Distillation was begun by heating the paraformaldehyde vessel to 110° in an oil-bath. During the removal of the first fraction by the pump, the condensing vessels were heated in a blow-pipe flame. It will be shown in a forthcoming paper that formaldehyde reacts rapidly with oxygen adsorbed on glass at 300°, so the above treatment should be such as effectively to free the surface from oxygen. The trap was now cooled in liquid air, and the stop-cock leading to the pump shut off. As the distillation proceeded, the rate gradually became slower and the temperature of the oil-bath could with advantage be raised to 120°. When sufficient solid had collected in the trap, the oil-bath was removed, the apparatus once more connected to the pump, and the trap carefully sealed off from the separator. By alternately removing and replacing the liquid air, the solid was allowed to melt and run to the bottom. The purity and stability of this first condensate suffice for most purposes, but specimens intended for measurements of physical properties were subjected to a second fractionation.

The preparation could be carried out with similar success if the separator vessel was immersed in calcium chloride-ice at  $-48^{\circ}$ , and the trap maintained at  $-78^{\circ}$  by carbon dioxide-ether. In this case, the formaldehyde condensed to a clear mobile liquid which slowly gelatinised if kept at  $-78^{\circ}$ , and at the end of a fortnight, no liquid was visible. The condensate in the first tube of the separator appeared to consist of a concentrated aqueous solution of formaldehyde. The second U-tube generally contained a viscous liquid which rapidly polymerised to a white solid, whilst only traces separated in the final trap.

Liquid formaldehyde prepared by this method shows no disposition towards rapid polymerisation. A specimen placed in a paraffin-bath at room temperature will rapidly boil away, leaving

only traces of polymeride. However, if it is kept for several hours at temperatures above  $-78^{\circ}$ , it begins to gelatinise. Clear liquid can at first be freed from the gel by shaking, but the latter becomes stiffer with time and no free liquid can be observed. Nevertheless, such a gel will evolve large quantities of monomeric gas, and when kept until there is no more vaporisation, only a relatively small fraction of the original specimen remains behind as solid polymeride. In the polymerisation of gaseous formaldehyde (Spence, *loc. cit.*), there is no evidence of the formation of any intermediate polymerides of low molecular weight. If the same is true of liquid formaldehyde, the gel system must consist of a solid phase and a pure liquid phase. Such a view would be in agreement with the above results and is entirely supported by measurements of the vapour pressure. All preparations of the liquid, whether clear and mobile, or highly gelatinous, would therefore appear to be equally satisfactory as sources of the pure gas.

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