

Keto-xylose was prepared for this investigation from aldo-xylose by a method similar to that described by Hassid *et al.*²

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¹ Johanson, R., *Nature*, **171**, 176 (1953); *Anal. Chem.* (in the press).

² Hassid, W. Z., Doudoroff, M., Barker, H. A., and Dore, W. H., *J. Amer. Chem. Soc.*, **68**, 1465 (1946).

Plastic Sulphur

LIQUID sulphur is well known to become highly viscous when heated above 160°C.; this viscous sulphur (like selenium) is easily supercooled. At room temperature the product resembles unvulcanized rubber and is called 'plastic sulphur'. This hardens at liquid air temperature to a brittle glass, vitreous sulphur. At this temperature it remains amorphous for an indefinite time; at room temperature, however, the plastic sulphur crystallizes within a few hours, the crystallization proceeding (as with selenium) from the outside to the inside. We have found that impurities and other factors have some curious effects.

The property of supercooling is completely destroyed by heating the viscous sulphur in a vacuum. The freshly vacuum-baked or vacuum-distilled viscous sulphur crystallizes within a few minutes, when poured into water or liquid air. Older preparations preserved in a vacuum by sealing them off in glass bulbs do the same. The admission of air to the hot preparations spoils them in the long run, but not immediately.

A second fact is that, conversely, the addition of as little as 1 per cent of a trivalent element (phosphorus or arsenic) greatly facilitates the supercooling, the doped mass eventually staying amorphous for at least some months at room temperature. Daylight has no influence on this stability; the exclusion of air, though not necessary, is favourable.

This influence of trivalent elements suggests that the usual supercooling is connected with the presence of some nitrogen in the preparation. The elimination of this nitrogen by vacuum-heating would explain why vacuum-heating of viscous sulphur prevents supercooling.

All the facts known to us may be explained by assuming in viscous sulphur the presence of very long chains, S_{∞} , instead of the S_8 -rings that are known to be stable at lower temperature, probably also in the liquid state below 160°. The long chains are presumably knitted together by the trivalent elements to form a network, more stable than the separate chains would be (compare the vulcanization of rubber).

The conception of long chains being built up above 160° also offers an explanation for the fact that traces of monovalent elements (1 per cent of bromine) greatly reduce the increase of viscosity at 160°, connected with their growth. We may suppose the halogen atoms to react with the terminal valencies of the chains at a rather early stage of their growth, thus

stopping further growth until full length is attained. Such inhibition is well known in the production of linear polymers.

The assumption that polymerization occurs at 160°, and that this polymerization is linear, is difficult to prove by direct means. X-ray evidence is inconclusive, because of its insensitivity to minor changes in molecular arrangement in the liquid state. The indirect evidence offered above and by other authors, however, is strong. Moreover, the theoretically well-founded divalence of sulphur makes long chains (scarcely distinguishable from big rings) the most probable molecular shape for explaining the phenomena.

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¹ Warren, B. E., and Burwell, J. T., *J. Chem. Phys.*, **3**, 6 (1935). Meyer, K. H., and Go, Y., *Helv. Chim. Acta*, **17**, 1081 (1934). Bacon, R. F., and Fanelli, R., *J. Amer. Chem. Soc.*, **65**, 639 (1943). Gee, G., *Trans. Farad. Soc.*, **48**, 515 (1952). Specker, H., *Z. Anorg. Allg. Chem.*, **261**, 116 (1950); *Angew. Chem.*, **65**, 299 (1953). Krebs, H., *Z. Anorg. Allg. Chem.*, **265**, 156 (1951); **272**, 288 (1953). Prins, J. A., and Dekeyser, W., *Physica*, **4**, 900 (1937); **6**, 1009 (1939). Prins, J. A., and Poullis, N. J., *Physica*, **15**, 696 (1949). Prins, J. A., and Schenk, J., *Plastica*, **6**, 216 (1953).

Effects of Commercial and Radiation-produced Hydrogen Peroxide

RADIOBIOLOGISTS and radiation chemists have for many years been aware of the fact that hydrogen peroxide formed during irradiation may play a significant part as an agent of the changes brought about by ionizing radiations. The method of checking has often been to expose the test material to concentrations of hydrogen peroxide comparable with those produced by radiation, and hence to deduce what part of the radiation effects must be ascribed to other agents. However, such experiments may be misleading if commercial hydrogen peroxide is used, since the stabilizer which is usually present may inhibit the decomposition of hydrogen peroxide into the intermediates which take part in the particular reactions being studied. Information is not always made available by manufacturers about the nature of the stabilizers used; my experience has shown that they are sometimes sufficiently volatile to distil over with the hydrogen peroxide, if redistillation is employed as a precautionary measure.

Where stabilizer is present, it may very well happen that the hydrogen peroxide will be less effective by a considerable factor than the same concentration produced in clean water by ionizing radiation. In the course of studies on the effects of radiation on dilute aqueous suspensions of bacteriophage, I have made use of hydrogen peroxide from various sources, and only occasionally has the commercial product had as much effect as that formed by radiation. For example, in one series of experiments the survival curve for phage exposed to 50 γ /ml. of a redistilled commercial hydrogen peroxide was matched by that for phage exposed, in otherwise identical conditions, to about 1 γ /ml. of hydrogen peroxide, produced by 15,000 r. of X-rays.