

protein. One might also suppose that one glycine molecule might be bound to another one already combined with the protein. It is not clear why such reactions should be slower than the formation of dioxopiperazin from glycine ethyl ester. The 'intra-globular' accumulation of dioxopiperazin molecules should have given a higher sedimentation constant (calculated from Talmud's figures,  $s = 4.02$ ) than we found. Talmud assumed that the whole volume of the egg albumin molecule could be filled with dioxopiperazin molecules. This disregards the volume taken up by the protein itself. The space available for non-protein materials inside the presumed globule must be much less than the total volume of the protein globule. The low value found for the diffusion constant probably must be explained by outside bound groups. If one presumes the egg albumin molecule to be spherical (which is very nearly true) and the bound groups to be placed symmetrically around it, the reduction of the diffusion constant from 7.76 to 6.6 means an increase of about 60 per cent in the volume.

It is therefore obvious that Talmud's experiments cannot be taken as an experimental proof of Wrinch's hypothesis, although they may be of interest for the understanding of protein structure and protein synthesis.

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<sup>1</sup> Talmud, D. L., *Compt. rend. Acad. Sci. U.R.S.S.*, **23**, 153 (1938). *Brit. Chem. and Physiol. Abstr.*, A, II, 42 (1939), and private communications.

<sup>2</sup> Wrinch, D. M., *Proc. Roy. Soc., A*, **160**, 59; *A*, **161**, 505 (1937); *Trans. Far. Soc.*, **33**, 1368 (1937); and several communications in NATURE.

<sup>3</sup> Fischer, E., *Ber.*, **31**, 433, 2868 (1901).

<sup>4</sup> Svedberg, T., NATURE, **139**, 1051 (1937); *Ind. and Eng. Chem., Anal. Ed.*, **10**, 113 (1938).

### Spontaneous Coagulation of Rubber Latex

So early as 1913, Whitby advanced the view that spontaneous coagulation in rubber latex takes place before decomposition processes begin<sup>1</sup>. Arguments against this view have since been advanced by several investigators, and the opinion at present generally held is that the coagulation of fresh latex is caused by formation of acid from the bacterial decomposition of the serum constituents.

Recent investigations made on latex of *Hevea brasiliensis* have provided confirmation of the view held by Whitby. Experiments were conducted throughout on latex obtained immediately after collection from the trees, which had been tapped three or four hours previously. The formation of ions from decomposition of latex was followed by conductivity measurements. The conductivity of latex did not change until coagulation was complete. This occurred 6-11 hours after collection of the latex, varying from sample to sample. The resistance of the conductivity cell increased after gel formation due to contact resistance on the electrodes.

The pH after coagulation (measured by Lyphan indicator strip) was only 0.2 lower than the average original figure of about 6.4. Decreasing the pH below 6 by the addition of phthalate-KOH buffer solutions had no effect on the rate of coagulation of the samples. After coagulation decomposition of latex constituents proceeds; but this bears no relation to the process of coagulation which is already complete.

Further support of Whitby's view was provided when strong antiseptics preventing bacterial decomposition were added to fresh latex without preventing spontaneous coagulation. The addition of 0.3 and 0.4 per cent sodium pentachlorophenate had no influence on the behaviour of latex as described. No decomposition nor any change in the pH value of 7 could be found in coagulated samples which were measured over a period of 3-6 weeks.

The exact nature of this process of coagulation is not known; enzymatic action on proteins may, however, be put forward as an explanation.

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<sup>1</sup> *Koll. Z.*, **12**, 151 (1913).

### Demonstration of the Participation of Free Radicals in the Rearrangement of Benzyl Phenyl Ether

It has been shown previously<sup>1</sup> that when benzyl phenyl ether is heated in quinoline at about 250°, the normal rearrangement of the ether to *o*- and *p*-benzyl phenols is accompanied by the formation of benzylquinolines and of toluene. It is now found that hydroxyphenyl quinolines are also products of this reaction, and that it is possible, by a careful control of the experimental conditions, to increase very considerably the yields of benzylquinolines and hydroxyphenyl quinolines at the expense of the normal products of the rearrangement.

This new evidence strongly supports the contention that the preliminary phase of the reaction is a dissociation of benzyl phenyl ether into benzyl and phenoxy groups. As both these groupings are found to attack the same positions in the quinoline nucleus, it seems unlikely that they react as ions having opposite charges. This result is consistent only with the view that the reactive centres of both groups are in the same electronic state<sup>2</sup>. This can only occur if the ether dissociates into free radicals.

This conclusion does not require the assumption of any special reaction of free radicals, except their ability to replace the hydrogen of the aromatic nucleus; it is based on experimental evidence which is considered to afford an independent and reasonably satisfactory demonstration of the existence of free radicals of short life in solution.

An extension of this investigation to other rearrangements is now in progress.

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<sup>1</sup> Hickinbottom, NATURE, **142**, 830 (1938).

<sup>2</sup> Bradley and Robinson, *J. Chem. Soc.*, 1254 (1932).

### A Fluoride with Pyrochlore Structure

THE formula of the rare mineral ralstonite is usually written  $(\text{Na}_2, \text{Mg})\text{F}_2 \cdot 3\text{Al}(\text{F}, \text{OH})_3 \cdot 2\text{H}_2\text{O}$ . This implies a replacement of  $\text{Na}_2$  by Mg. X-ray investigation of this mineral shows that it belongs to the space-group  $O^h - Fd\bar{3}m$  and that the edge of the unit cube has a length of 9.87 Å. By recalculation from the best available analysis (Penfield and Harper, 1886), it can be shown that a unit cube contains on the average 48 (F,OH), 16 (Al,Mg), 2.7 Na and 7  $\text{H}_2\text{O}$ . The structure is similar to that