

To test the hypothesis by this means, 2-chloropyrimidine was heated with ammonia (enriched by nitrogen-15) in ethanol for 2 hr. at 120° C. to give 2-aminopyrimidine labelled in the amino group. This was treated with methyl iodide¹, and the resulting compound (I) (hydroiodide, of melting point 251° C. undepressed by admixture with unlabelled material) was rearranged¹ in hot alkali to 2-methylamino-pyrimidine (II). Hydrolysis of the sublimed material (melting point 58° C.; published 59–60° C.) with *N* hydrochloric acid at 160° C. for 6 hr. gave 2-hydroxypyrimidine (III) (melting point 178° C.; published¹³ 178–80° C.) and after making the residual solution alkaline, methylamine was isolated using steam-distillation and collected as its picrate (melting point 207° C., undepressed by authentic material). Mass-spectrometric examination of nitrogen samples prepared by burning compound (III) and the methylamine picrate showed a strong nitrogen-15 enrichment in nitrogen from the 2-hydroxypyrimidine, but none in nitrogen from the picrate. The rotation hypothesis for the mechanism of rearrangement was thus valid.

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The Sodium Silicate – Ferrous Hydroxide System

WE have reported earlier¹ the occurrence of a point of inflexion at *pH* 10.75 on the hydrolysis curve of a 0.01 *M* sodium silicate solution which was attributed to the formation of the trihydroxy – orthosilicate ion, but we were unable to detect with certainty a point on this curve corresponding to the final decomposition of this ion to orthosilicic acid, Si(OH)₄. An investigation of the sodium silicate – ferrous hydroxide system has shed new light on this problem. It is known that controlled oxidation of ferrous hydroxide between *pH* 5.2 and 11.5 yields magnetite^{2,3}, and it has also been established⁴ that silica prevents the formation of magnetite from solution. One could therefore expect a systematic investigation of the sodium silicate – ferrous hydroxide system over a wide *pH* range to assist in clarifying the behaviour of silicic acid.

The experimental procedure involved addition of sodium silicate solutions to 0.005 *M* suspension of precipitated ferrous hydroxide, yielding a final ratio of sodium silicate to ferrous hydroxide of 0.4 : 1 (excess ferrous hydroxide) and 1.5 : 1 (excess silicate) respectively, and subsequent oxidation of two-thirds of the iron present with 0.3 per cent hydrogen peroxide; *pH* of the mixture was varied between 5.1 and 13.8 and the entire operation carried out under a nitrogen atmosphere at 25 ± 0.02° C. Samples were tested for magnetic behaviour and submitted to X-ray analysis using the powder diffraction method.

We found that, below about *pH* 10.7, magnetite is not formed in any appreciable quantities, whereas above this point it is the major product together with some very finely divided α-ferrous oxide. On the other hand, an analogous procedure in the absence of silicate ions led us to establish *pH* 5.25 as the lower limit for the formation of magnetite.

It would therefore appear that *pH* 10.7 marks the end of hydrolysis of the dihydroxy – orthosilicate ion in 0.002–0.007 *M* sodium silicate solutions:



Such freshly formed silicic acid in aqueous solution, being in an active condition⁵, will be readily adsorbed by ferrous hydroxide particles and thus prevent the formation of magnetite below *pH* 10.7. This finding can be related to a recent observation⁶ that at *pH* 8.5 the formation of magnetite from solution is a solid phase reaction.

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Reaction of Phosphorylating Agents with 2-Methyl-Δ²-Oxazoline

DEGRADATION of esteratic enzymes which have been inhibited with diisopropyl phosphorofluoridate (DFP) yields serine phosphate¹, although serine itself is completely unreactive to DFP². Kinetic and other evidence³ suggests participation of the imidazole ring of a histidine moiety in the phosphorylation reaction, although it is not known if the ring is the initial site of phosphorylation or whether it catalyses phosphorylation of the serine. Rydon⁴ has postulated that a Δ²-oxazoline is present in the enzyme which on phosphorylation yields an O-phosphoryl serine residue. This hypothesis was based on the results of Porter *et al.*⁵, who showed that 2-aminoethyl phosphate could be isolated from the reaction of 2-methyl-Δ²-oxazoline (I) and DFP in aqueous solution. Since acylating agents⁶ react with I to give stable N-acyl derivatives, and since 2-aminoethyl phosphate was isolated by Porter *et al.* following acid hydrolysis of the product (conditions under which N → O migration of phosphoryl groups is known to occur⁷) the reaction