As regards the colour formation with *p*-dimethylaminobenzaldehyde, it is known that α-amino carbonyl compounds self-condense to form dihydropyrazines or pyrazines. The dihydropyrazine derivative is assumed to form with *p*-dimethylaminobenzaldehyde the chromophore in the Ehrlich reaction.

It may be pointed out that another source of humin-like substances from an amino-acid – hexose mixture arises from D-glyceraldehyde, dihydroxyacetone and methylglyoxal, produced under alkaline conditions from free hexoses. Thus D-glyceraldehyde rapidly combined with L-lysine at 20° C. to give a dark-brown product.

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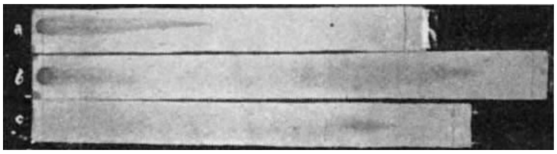
Chromatography of Proteins

WE have been concerned with the chromatographic separation of proteins and have developed a simple method of location of proteins on a paper chromatogram or a cellulose column. We have utilized the fact that acid dyes have an affinity for protein fibres but not for cellulose. The developed chromatogram is treated with an acid solution of a suitable dyestuff, preferably warmed for a few minutes, then rinsed in water, when the proteins appear as coloured spots or streaks on a white background. Amino-acids and peptides are not stained.

The selection of dyestuff is important; one having high affinity for protein fibres and not staining cellulose is necessary. There are very many such dyes; we have had excellent results with Solway Purple, among others. A one- or two-dimensional paper chromatogram, after drying, is immersed in a 0·05 per cent solution of the dye containing 0·5 per cent sulphuric acid in a photographic developing dish, at a temperature of 50–90° C. After rocking the dish for about five minutes, the dye solution is poured off and the paper washed in several changes of warm water and finally dried. The proteins show up as violet-coloured patches on the chromatogram (see accompanying photograph).

This dyeing property can be utilized in various ways. For example, we have studied the movement of proteins along the chromatogram, using different liquids. Also, when the eluate from a column is collected in fractions, a drop of each fraction can be placed on a sheet of filter paper, which is then dried and treated as described. The protein-containing fractions will show coloured spots on the paper.



Blood serum developed with phosphate buffer *p*H 9 containing ammonium sulphate to (*a*) 70 per cent saturation; (*b*) 50 per cent saturation; (*c*) 30 per cent saturation. The line marks the solvent front

In the case of cellulose columns, the column can also be extruded, and small samples taken at intervals along the column from the outside. These samples may be moistened, placed on disks of filter paper, dried and then dyed. Those containing protein will give coloured spots, and the appropriate sections can then be cut out from the column and eluted separately.

The extension of the method to the quantitative estimation of the different protein fractions is being studied.

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A Conversion Series for Organosilicon Halides, Pseudohalides and Sulphides

RECENTLY organosilicon *iso*cyanates and *iso*thiocyanates have been prepared by interaction of the corresponding organochlorosilanes, $R_x\mathrm{SiCl}_{(4-x)}$, with silver cyanate and thiocyanate respectively[1], and alkyl(*iso* ?)cyanosilanes have been prepared by interaction of alkyliodosilanes with silver cyanide[2]. It has now been found that by boiling triethylhalogenosilanes, triethylpseudohalogenosilanes, and hexaethylthiodisiloxane under reflux with excess of the appropriate silver salt, transformations may be carried out along the series

$$\mathrm{Et_3SiI} \rightarrow (\mathrm{Et_3Si})_2\mathrm{S} \rightarrow \mathrm{Et_3SiBr} \rightarrow \mathrm{Et_3SiNC} \rightarrow \mathrm{Et_3SiCl} \rightarrow \mathrm{Et_3SiNCS},$$

it being possible to convert a compound to any other on the right of it, either directly or through any of the intervening compounds. A compound cannot be appreciably converted to a compound on the left of it by this method.

Calculation shows some of the reactions concerned to be markedly endothermic, and it seems that neither the overall energy change in a particular reaction, nor the relative solubilities of the silver salts concerned (assuming these solubilities to be in their usual order), govern the direction of the change. It is suggested that the relative strengths of the Si—*X* bonds may determine this direction. Certainly, in those cases in which the bond-energies are known[3], namely, Si—I, 51·1; Si—S, 60·9; Si—Br, 69·3; Si—Cl, 85·8 (k.cal./mole), there is agreement with the experimental series above. The reactions may be considered to bear some analogy to the ionic exchange reactions of organic chemistry; the silicon atom is very susceptible to nucleophilic attack, and it would be expected that the nucleophilic activity of the ions concerned, and hence the direction of the reactions, would be related to the Si—*X* bond-strengths. If the series does, in fact, reflect the order of bond-strengths, it may be expected to be of significance in other reactions.

Salts other than those of silver may be employed in the conversions; lead chloride and cadmium chloride have been used, for example, to convert hexaethylthiodisiloxane to triethylchlorosilane; but the silver salts seem to be generally satisfactory. For trimethylsilicon derivatives the series

$$Me_3SiI \rightarrow (Me_3Si)_2S \rightarrow Me_3SiCl \rightarrow Me_3SiNCS$$

has so far been confirmed, and the series given for triethylsilicon derivatives may prove to be of general applicability. The series will probably be extended to include electronegative groups other than the halides, pseudohalides and sulphide listed.

Hexaethylthiodisiloxane (b.p. 278–279°/750 mm.) and hexamethylthiodisiloxane (b.p. 162·5°/735 mm.) are the first organosilicon sulphides to be reported, and are of particular interest in view of the present-day importance of siloxanes. The weakness of the Si—S bond relative to the Si—O bond suggests, however, that the behaviour of thiosiloxanes will not show many analogies to that of siloxanes.

The investigation is proceeding, and a full discussion of the results will be submitted for publication elsewhere.

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Mechanism of the Nitration of Starch

In studying the nitration of maize and potato starch, we observed that: (*a*) a mixture of nitric and sulphuric acids, containing a high proportion of pseudo-nitric acid, namely, an equimolecular mixture of water, nitric and sulphuric acid[1], leads to the formation of nitric esters of low nitrogen content (7·1 per cent); (*b*) in the nitration of starch by means of such mixed acids containing decreasing quantities of water and increasing amounts of free sulphur trioxide, the degree of nitration of starch is controlled by the proportion of water and sulphur trioxide, respectively, in the nitrating mixture. Nitrates of starch, containing about 13 per cent of nitrogen, could be obtained easily when mixtures of pure nitric acid and oleum[2] (2–3 per cent sulphur trioxide) were used. A similar observation has been reported by Fabel[3] in the case of the nitration of cellulose. Caesar *et al.*[4] have also found that starches, cellulose and disaccharides are completely and rapidly nitrated by nitrogen pentoxide and that the nitrates thus produced have an unusually high nitrogen content (about 13·9 per cent).

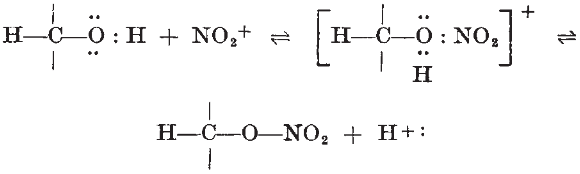
These observations suggest that in the above nitration reaction it is not pseudo-nitric acid which represents the active agent[5], but rather a strongly electrophilic molecular species. It is submitted that the active agent is the positive nitronium ion (NO_2^+) recently identified as the nitrating species in the nitration of aromatic systems[6]:

$$HNO_3 + 2H_2SO_4 \rightleftharpoons (NO_2^+) + H_3O^+ + 2HSO_4^+.$$

Conditions which favour the formation of the nitronium ion led to nitrates of high nitrogen content. One would also assume that nitrogen pentoxide reacts as nitronium ion, so that the structure of $(NO_2)^+(NO_3)^-$ should be ascribed to its 'reactive state'[7].

It may be recalled that Chedin[8] and Chedin and Pradier[9] observed for nitrogen pentoxide a different Raman spectrum in chloroform or carbon tetrachloride on one hand, from that in sulphuric acid or the solid state on the other. They explained the difference on the hypothesis that the group NO_2^+: or a polymer of the pentoxide is present in the sulphuric acid solution.

One is tempted to suggest that the formation of the nitrates is due to an attack of the nitronium ion on a lone electron pair of the hydroxyl oxygen, followed by elimination of a proton from the intermediate product.



$$H{-}\overset{|}{\underset{|}{C}}{-}\ddot{\underset{\cdot\cdot}{O}}:H + NO_2^+ \rightleftharpoons \left[H{-}\overset{|}{\underset{|}{C}}{-}\underset{\underset{H}{\cdot\cdot}}{\ddot{O}}:NO_2\right]^+ \rightleftharpoons H{-}\overset{|}{\underset{|}{C}}{-}O{-}NO_2 + H^+:$$

Obviously, the presence of water would enhance the reversal of the primary attack.

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Dielectric Properties of Solid Hydrogen Bromide

We have recently extended the measurements of Smyth and Hitchcock[1] on solid hydrogen bromide both in frequency and temperature-range, and our results given in terms of the real (ε′) and imaginary (ε″) parts of the dielectric constant agree where the comparison is possible with those of the above authors.

The values of ε′ and ε″ as a function of frequency, with the temperature as a parameter, are shown in the accompanying diagram, and we see that there is a variation of dielectric properties with frequency, for the frequency-range covered, only for temperatures below that of the lowest transition (~ − 183° C.). The measurements were made at constant temperature and variable frequency, and for the series of measurements the temperature was not allowed to rise above − 184° C., since the measured values are not exactly reproducible after passage through the transition. Moreover, the values of ε′ below − 184° C. may vary by as much as 25 per cent according to the way of freezing the liquid hydrogen bromide in the dielectric cell. Consequently the