Spontaneous Gelation of Alkaline Casein Dispersions

IN a communication in *Nature* of February 10, Plomley, Higgins and Hayes describe the dependence of viscosity and rate of gelation on pH. Their results are in general agreement with those obtained in this laboratory for lactic casein and denatured peanut protein spinning dopes; dopes to be spun into fibres must obviously have considerable stability to allow time for filtration and de-aeration.

The authors mention that search for the specific groups concerned in the gelation process is proceeding. There are a number of indications that the specific group concerned in gelation is the sulphhydryl group¹. Oxidation catalysed by oxidative enzymes increases the tendency to gel:

Milk casein and peanut protein dopes containing sodium sulphide are much more stable than dopes of similar alkalinity not containing sodium sulphide; the latter agent would inhibit the formation of disulphide bonds.

There is a pH (c. 12.5) giving maximum stability for both milk casein and peanut protein dopes; if milk casein dope containing c. 20 per cent lactic casein and 0.50 per cent free caustic soda is made more alkaline by the addition of 50 per cent more caustic soda, the dope becomes a gel after two days at 25° C.; but if the additional alkali is in the form of sodium sulphide, the change in viscosity is quite small. At very high alkalinity, the ultimate decline in viscosity is likely to be due to hydrolysis.

Thomson and Traill² have explained the peculiar behaviour of peanut and other seed protein dopes in terms of denaturation and chain rupture. Both these factors are important; but the irreversible nature of the gel suggests cross-linkage formation, and the most likely link appears to be the well-known disulphide bond. In comparing denatured peanut protein dopes with milk casein dopes, both types of dispersions show similar sequences of viscosity changes; but the peanut dispersions are more sensitive to change, and this would be in accordance with their higher cystine content.

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¹ Wormell, *J. Text. Inst.*, **41**, 16 (1950); B.P. 14559/1949 (Courtaulds), Ltd.

² Thomson and Traill, *J. Soc. Chem. Indust.*, **64**, 229 (1945).

Electrolytic Oxidation and Reduction of some Pyridine Compounds

As part of an investigation for developing satisfactory procedures of preparing 2-, 3- and 4-pyridine-aldehydes, attention was turned to the electrolytic oxidation and reduction of pyridine compounds. After consideration of commercially available pyridine derivatives, studies were made of the electro-oxidation of 2-, 3- and 4-picoline and of 2-vinylpyridine and the electro-reduction of picolinic, nicotinic and isonicotinic acids. Inasmuch as the results do not show promise of being successful with respect to the primary object, the work has been abandoned. Nevertheless, some of the observations are interesting, although several points need further inquiry.

Other than minor modifications for electrolyses carried out at elevated temperatures, the basic arrangement consisted of a clay porous cup, for one cell compartment, sitting or suspended in a beaker, which served as the other cell compartment. A mechanical stirrer was used for agitation. More than a hundred electrolyses were conducted to observe the effect upon the yield of aldehyde when varying separately the type of electrodes, amperage, current-density, applied E.M.F., temperature, concentration of pyridine derivative, time of electrolysis, type of electrolyte at anode or cathode, or addition of an agent to precipitate the aldehyde as it is produced.

Aliquots from the solutions in the cathode compartment in reductions and from the anode compartment in oxidations were analysed for carbonyl and nitrogenous products. A quantitative determination of the former was made by producing and weighing the precipitated 2,4-dinitrophenylhydrazone, and its qualitative identification was made through mixed melting points with authentic samples. Ammonia was detected through its picrate by mixed melting points with known samples of ammonium picrate.

PRODUCTS OBTAINED IN THE ELECTRO-REDUCTION OF *iso*NICOTINIC ACID

Type of cathode	Applied E.M.F. (volts)	Product
Tin foil	6	23.4% CH ₃ CH ₂ CHO
Lead plate	6	Identity unknown*
Platinum black	6	10.7% (CH ₃) ₂ CHCHO
Mercury-pool	5	28.7% "
"	4	21.4% "
"	3	(CH ₃ CH ₂) ₂ CHCHO†

* Known not to be any of the other aldehydes in this table.

† Identity not conclusive.

In the reductions, the surprising observation was the profound effect that the type of cathode and applied E.M.F. has upon the mode of cleavage of the nucleus of *isonicotinic acid*. In the accompanying table are listed the aldehydes isolated as their 2,4-dinitrophenylhydrazones in the reduction of *iso*-nicotinic acid. It is noteworthy that the pyridine nucleus is cleaved in various ways, depending upon the conditions. In each case ammonia was also produced. Wibaut and Boer¹ and F. Sorm² have