2953

The rôle of water in the starch iodine reaction.

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A number of investigators[1, 2, 3] have reported that "dry" starch will not react with iodine to produce the well-known blue substance, starch iodide.

Starch is a very hygroscopic material,[4, 5] and like other hygroscopic substances, when in contact with the atmosphere, will tend to absorb water until the vapor pressure of the absorbed water is in equilibrium with the vapor pressure of the surrounding air.[6] Many of the researches involving "dry" starch were carried out with starch in more or less complete moisture equilibrium with the atmosphere, hence by no means really dry.

The conditions of preparation, storage, and other treatment which affect moisture content, of the starch used should be fully described in work of this sort.

Since the literature indicates that starch at a certain degree of dryness will no longer yield blue starch iodide when treated with iodine, it seemed worth-while to determine approximately the water concentration necessary that this reaction may take place.

In the following investigation the starches used were prepared according to the method of Alsberg and Rask[7] and ground after the method of Alsberg aand Perry,[8] and then stored for varying periods of time in reagent bottles at room temperatures. Such preparations were of course in moisture equilibrium with the air in the containing vessel.

In ground starch the comparatively dense outer layer of the starch grain, which as Denniston[9] pointed out, reacts more slowly

[1] Tomlinson, C., *Phil. Mag.*, 1885, xx, 168.

[2] Stocks, *Chem. News*, 1887, lvi 212; 1888, lvii, 183.

[3] Andrews and Goettsch, *J. Am. Chem. Soc.*, 1902, xxiv, 865.

[4] Archbold, *J. Soc. Chem. Ind.*, 1887, vi, 83.

[5] Reichert, Carnegie Inst. Wash. Pub. No. 173, Pt. 1, 1913, p. 167.

[6] Fisher, E. A., *Proc. Roy. Soc. A.*, 1923, ciii, 139.

[7] Alsberg and Rask, *Cereal Chem.*, 1924, i, 7.

[8] Alsberg and Perry, PROC. SOC. EXP. BIOL. AND MED., 1924, xxii, 60.

[9] Denniston, *Proc. Wis. Acad. Sci.*, 1907, xv, 664.

with iodine than the inner portion of the grain, is cracked and chipped, and are more favorable for rapid formation of starch iodide than when the intact grain is used.

The technique employed was essentially that of Gobley.[1]

Samples of ground wheat and potato starches were placed on separate glass slides and spread out in a thin layer with a spatula. These were then placed in a small, empty dessicator. Another slide, containing more than enough iodine crystals to saturate the dessicator with iodine vapor was also placed in it, and the dessicator was closed and allowed to stand 24 hours at room temperature.

On examination after 24 hours neither starch showed a trace of blue color. Both were brown, due to condensed and probably some adsorbed iodine.

Above experiments were repeated. After 24 hours the results noted above having recurred, water was added to the bottom of the dessicator in more than sufficient amount to saturate the system. Neither the starch nor the iodine were in contact with liquid water. The system was closed and allowed to stand. In less than half an hour traces of blue appeared on the starches, and on examination 24 hours later both starches were deep blue in color. The starch particles at this time adhered to one another, but when any mass was broken up it was observed that the blue color extended homogeneously throughout.

Starches and iodine were arranged in a dessicator as above, but enough water was added to the system to saturate it at the same time that the starches and iodine were put in. In a short time traces of blue were apparent, and after 24 hours both starches showed a deep blue-black color. It should be noted that there seemed to be no difference in final shade between potato and wheat starch iodide.[5]

Samples of wheat and potato starches were added as before to a system already saturated with both water and iodine vapor. The results differed only in a more rapid development of blue color.

All the above experiments were repeated using the same starch preparations as above, but first exposing the samples taken directly to the laboratory air for 24 hours. This procedure did not cause any difference in results.

The experiments show that there is a threshold concentration of moisture requisite for the starch iodine reaction. Furthermore, since the moisture content of the starch is a function of

the environmental free water concentration, this latter is the controlling factor in so far as the aqueous features of the reaction are concerned. It has been known for many years that there is a threshold concentration of iodine necessary for the reaction.[10]

The value of this threshold water concentration lies between that producing saturation pressure at approximately 22 degrees Centigrade, and above the water concentration present usually in the laboratory air of the Department of Chemistry at Stanford University during the clear season, when the humidity averages below 50 per cent.

At the threshold concentration of iodine, water being in excess, the formation of starch iodide as measured by the development of the blue color, is very rapid. At the threshold concentration of water, iodine being in excess, the reaction seems to be comparatively slow. However, it may be that other factors are concerned in the latter case.

[10] Meineke, *Chem. Ztg.*, 1894, xviii, 157.