The Stability of Dry Potassium Ferrocyanide

BY ROBERT B. LOFTFIELD[1] AND ELIJAH SWIFT, JR.

In the course of a previous investigation,[2] it was noticed that sometimes dry potassium ferrocyanide undergoes a slight decomposition. Since this salt is one of the few quadrivalent salts that is sufficiently stable to be useful in precise electrochemical investigations[3] where the effect of ionic charge on the properties of solutions is being studied, it seemed of some importance to determine the conditions under which decomposition takes place.

Mallinckrodt reagent grade potassium ferrocyanide was precipitated from saturated solution at 0° by adding an equal volume of cold 95% alcohol. The crystals were allowed to grow for several hours and then were centrifuged and washed with cold 95% alcohol. This process was repeated and the salt was dried by sucking off the excess alcohol with a water pump. After standing in a clear glass bottle exposed to the ordinary laboratory light for over a year, no change in color could be observed by comparison with freshly prepared salt, and no odor of hydrogen cyanide was perceptible in the bottle.

The salt was dehydrated as in previous investigations[3] in order to get a sample whose exact composition would be known. About 0.5 g. of the salt was placed in a platinum boat in a Richards bottling apparatus and a slow stream of nitrogen was allowed to flow over the sample while heating to 90°. The nitrogen was removed with a water pump and the tube flushed out several times with nitrogen and finally left evacuated for one to two hours while the temperature was maintained at 90–100°. The tube was then filled with nitrogen and the salt cooled in a slow stream of the gas. This method of preparing the salt was found by Jones and Jelen[3a] to give material of constant weight.

Fabris[4] has stated that there is a considerable loss of cyanide[5] when this salt is heated above 50° in air. To check this statement, samples of salt were heated to 100° for three hours in a slow stream of air, the effluent gas being passed through a solution of sodium hydroxide. The Prussian blue test applied to this solution was negative, showing that less than 0.01% of the salt was lost as cyanide in this process. Negative tests for cyanide were also obtained when samples of salt were heated in a slow current of nitrogen, using the Prussian blue test and the specific ferric thiocyanate test.[6] It seems evident that this salt may be dehydrated safely at 100°, although decomposition will take place at higher temperatures.[7]

After the dehydrated salt had come to room temperature, half of the boat was covered with platinum foil and the salts exposed to illumination. After two hours of illumination with a "Pointalite" bulb and forty hours' illumination with a 200-watt tungsten bulb 15–20 cm. above the surface, no change in the color of the salt was observed. The tube was then flushed out several times with dry oxygen and the process repeated. After about forty hours of exposure a slight change in the color of the salt was observed, and after seventy-two hours there was a decided greenish-blue color on the surface of the salt. This color was much less pronounced underneath the foil where the light could reach the salt only indirectly; while another sample kept in dry oxygen in the dark for seventy-two hours failed to show any color change whatever. Presumably the reaction involves the formation of Prussian blue, but the amount of material formed was too minute to be analyzed readily, and it was not thought worth while to investigate this reaction further. The test was repeated by placing a fresh sample in dry oxygen in direct sunlight, and the same result was observed after one or two hours' exposure. A control sample of the hydrated salt showed no reaction whatsoever under any of the above conditions.

Another sample of the anhydrous salt was placed in an atmosphere of moist oxygen and exposed to illumination. No reaction was observed, probably because the salt picked up moisture and went into the more stable hydrated form before any appreciable photochemical reaction could take place.

To determine whether the anhydrous salt is deliquescent, a sample was placed in a container saturated with water vapor at room temperature (30°). The salt quickly picked up even more than the three moles of water normally present and deliquesced to a sticky mass. Microscopic examination of the dehydrated salt showed that the crystals are practically intact after dehydration, since there is no change in the gross form and the smallest crystals appear quite as clear as before dehydration. Larger, clear crystals become translucent after dehydration, due to their breaking up into smaller units, but they also retain the same shape, and do not break up into an amorphous white powder.[8] It is probable that the dehydrated material will go back to the same photochemically stable trihydrate on exposure to moisture.

On the basis of this investigation, we believe that potassium ferrocyanide is sufficiently stable to be used in precise investigations if the following conditions are observed:

1. The salt must not be dehydrated at temperatures greater than 100°.
2. The dehydrated salt must be kept out of contact with moisture before and during weighing, but not necessarily after.
3. The dehydrated salt must be kept in the dark to prevent decomposition.

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[1] Harvard National Scholar, '41.

[2] E. Swift, Jr., THIS JOURNAL, **60**, 728 (1938).

[3] (a) Grinnell Jones and F. C. Jelen, *ibid.*, **58**, 2561 (1936); (b) Grinnell Jones and R. E. Stauffer, *ibid.*, **58**, 2558 (1936).

[4] Fabris,, *Gazz. chim. ital.*, **61**, 527 (1931).

[5] Autenrieth, "The Detection of Poisons," P. Blakiston's Son and Co., Philadelphia, Penna., 1921, p. 21, states that many other substances will react in the same way as hydrogen cyanide, and that the test used by Fabris is not conclusive evidence of the presence of this gas.

[6] According to McAlpine and Soule, "Qualitative Chemical Analysis," D. Van Nostrand Co., New York, N. Y., 1933, p. 460, the thiocyanate test is good to 1 p. p. m. or better.

[7] One sample of salt heated to 140° lost about 0.1% of cyanide.

[8] Roscoe and Schorlemmer, "Treatise on Chemistry," The Macmillan Co., New York, 1907, Vol. II, p. 1230.

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Changes in the Physical Properties of Regenerated Cellulose by Liquid Ammonia

BY RICHARD G. ROBERTS

During the dialysis of proteins and hormones contained in bags made from regenerated cellulose film and placed in liquid ammonia, it was observed that the bags changed in size and in flexibility. Therefore, a series of comparative tests on some of the physical properties of the film and ammonia-treated film was made. The film used in these tests was du Pont Cellophane number 600.

The film was cut into strips of convenient size and placed in a Dewar flask. Liquid ammonia, previously dried over metallic sodium, was added to immerse the film sample completely. The film was not previously dried by us. The Dewar flask was tightly stoppered, and attached to a mercury seal. The liquid ammonia boiled off in about twenty-four hours, and any excess ammonia gas was removed by a vacuum pump.

Physical properties showing an increase:	
Tear strength (Elmendorf test)	200.0%
Tensile strength	70.6%
Thickness (flat micrometer)	152.4%
Weight (per unit area)	27.3%
Physical properties showing a decrease:	
Length (with grain)	8.3%
Width (cross grain)	17.8%
Area	24.7%

Ratios: Increase of tear strength to decrease in area, approximately 8 to 1. Increase of tensile strength to decrease in area, approximately 3 to 1.

It has been shown that bags made from regenerated cellulose film may be used conveniently for dialyzing experiments in liquid ammonia, although some space must be allowed for shrinkage.

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The Specificity of the Fermentation Test for Vitamin B_1

BY ALFRED S. SCHULTZ, LAWRENCE ATKIN AND CHARLES N. FREY

The fermentation method for the determination of vitamin B_1[1-3] has been in successful operation for some time. The effect of 2-methyl-5-ethoxymethyl-6-aminopyrimidine has been described.[2] We have assayed a wide variety of substances such as non-autoclaved yeast, rice polish, vitamin pills and concentrates, solutions of crystalline vitamin, and milk, and no evidence of the interfering substance has been found. In an investigation on the metabolism of vitamin B_1,[4,5] we found reason to believe that a portion of the fermentation stimulating effect of urine is not due to vitamin B_1. While this did not appear to alter the significance of the results, it was thought very desirable to find a method for differentiating between the intact vitamin molecule and any possible breakdown product. A way of doing this has been found in the differential oxidation of the vitamin B_1 in the presence of the aminopyrimidine.

Alkaline ferricyanide in the cold will readily oxidize the vitamin to thiochrome. Preliminary experiments with a sample of thiochrome obtained from Merck and Company showed it to be inactive in the fermentation reaction. The aminopyrimidine is more resistant to oxidation and it is a simple matter to oxidize B_1 preferentially when present in addition to aminopyrimidine. A solution containing 8 gamma of the aminopyrimidine and 8 gamma of thiamin hydrochloride in a volume of 35 ml. was treated with 2.5 ml. of 1% $K_3Fe(CN)_6$ and 2.5 ml. of 50% NaOH. After standing at room temperature for five minutes the solution was neutralized with dilute sulfuric acid and made to 100 ml. A 25-ml. aliquot of this was tested in the usual manner by gas test. It gave a stimulation which corresponded exactly to 2 gamma of the aminopyrimidine (*i. e.*, the B_1 was destroyed) Parallel experiments showed that the neutralized oxidizing solution was without influence on controls with either thiamin hydrochloride or aminopyrimidine.

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(1) A. S. Schultz, L. Atkin and C. N. Frey, THIS JOURNAL, **59**, 948 (1937).

(2) A. S. Schultz, L. Atkin and C. N. Frey, *ibid.*, **59**, 2457 (1937).

(3) A. S. Schultz, L. Atkin and C. N. Frey, *ibid.*, **60**, 1514 (1938).

(4) A. S. Schultz, R. F. Light and C. N. Frey, *Proc. Soc. Exptl. Biol. Med.*, **38**, 404–406 (1938).

(5) R. F. Light, A. S. Schultz, L. Atkin and L. J. Cracas, *J. Nutr.*, **16**, 333 (1938).