

(-10 after each), and 0.81624 is the density at 0°. This equation fits the values of Perkin (15°, 25°) very closely.

The refractivities can be calculated with more certainty, since Doroshevski and Dvorzhanchik showed that the formula $\eta_t = \eta_o / (1 + kt)$ holds for the common alcohols. Where the refractivity has been determined for two temperatures, a value for k can be calculated. We have used for *n*-propyl alcohol, $k = 0.032368$ (values of D. and D.); *iso*-propyl alcohol, 0.032850 (authors' values); *iso*-butyl alcohol, 0.03269 (D. and D.).

No values are given in Table II for methyl-*iso*-butyl-carbinol. It has been prepared by Skita and Ritter,¹ Pickard and Kenyon,² Guerbet,³ and others, but, although its boiling point has been known to be in the neighborhood of 131°, no determinations of its density or refractivity are recorded.

The authors acknowledge with pleasure the courtesy of the U. S. Bureau of Standards in providing opportunity for the first boiling point tests with one of their resistance thermometers, and, in particular, their indebtedness to Miss Amelia K. Benson, with whose assistance the tests were made.

They also take pleasure in acknowledging their indebtedness to the Warren Fund of the American Academy of Arts and Sciences for a grant which covered the cost of materials for this work as well as for the preparation of several alcohols on which the work is not yet completed.

NITROTARTARIC ACID.

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Although nitrotartaric acid is the raw material of the important dye tartrazine, it has not been the subject of much published work; it is, however, a very interesting substance. It was first prepared by Dessaignes,⁴ by dissolving tartaric acid in strong nitric acid, and adding sulfuric acid to the mixture. He found it a rather unstable compound, and described its decomposition products quite accurately, although he overlooked the most important one, *viz.*, dioxy-tartaric acid. This reaction was discovered by Kekule.⁵ Dihydroxy-tartaric acid behaves like a diketone, and it is a condensation product of this diketone with phenylhydrazine sulfonic acid which forms the dye tartrazine.

There would seem to be little doubt, from its method of preparation, that nitrotartaric acid is really what its name implies, *viz.*, the nitric ester of tartaric acid; yet it is usually referred to with quotation marks around the "nitro," or as "the so-called nitrotartaric acid." Its actual relation-

¹ Skita and Ritter, *Ber.*, **43**, 3397 (1910).

² Pickard and Kenyon, *J. Chem. Soc.*, **99**, 56 (1911).

³ Guerbet, *Compt. rend.*, **149**, 129 (1909).

⁴ Dessaignes, *ibid.*, **54**, 731 (1852).

⁵ Kekule, *Ann.*, **221**, 245 (1883).

ship to tartaric acid could only be brought out by *reducing* agents, such as ammonium sulfide; other reagents gave either *dihydroxy*-tartaric acid, or its decomposition products. It was an open question, therefore, whether nitrotartaric acid is not really a derivative of dihydroxy-tartaric acid, and thus an oxidation product rather than an ester.

The Constitution of Nitrotartaric Acid.

It is very difficult to dehydrate nitrotartaric acid completely; if the material is left exposed to air, it slowly takes up more moisture, loses nitrous acid, and changes over to the dihydroxy acid. If the slightly moist nitro acid is stored in a stoppered vessel, on the other hand, the brownish fumes, which appear at first, soon vanish; and after an interval of several weeks, the bottle contains *nitric* acid fumes, and a hard crust which proves to be chiefly tartaric acid.

The hydrolysis of nitrotartaric acid into its original components may be hastened considerably. One and ninety-three hundredths g., moistened with one drop of water in a test-tube, showed nitric fumes after 4 days; after 6 days, tartaric acid was determined by the Goldenberg method, and 1.07 g. found, 89% of the amount calculated. The same quantity of nitro acid was moistened with one cc. of strong nitric acid, containing 0.3 g. of water (just sufficient for complete hydrolysis) when 1.12 g. of tartaric acid was found, 94% of the theoretical yield. The reaction in this latter case completed itself overnight.

The extent of this acid hydrolysis is strongly influenced by the proportion of water present. Thus, when 2.00 g. of nitro acid was allowed to stand with 7 g. of water and 2 g. of nitric acid, only 0.15 g. of tartaric acid was found, a 12% yield, and when still larger proportions of water are used, only traces of tartaric acid make their appearance.

Tartaric acid is also produced by the action of a few drops of strong hydrochloric acid or of moderately diluted sulfuric acid. There is little doubt, therefore, that nitrotartaric acid is a true nitric ester in the presence of high concentrations of mineral acids.

Preparation and Properties of Nitrotartaric Acid.

Preparation.—To prepare nitrotartaric acid, it is not necessary to use fuming nitric acid, as Dessaignes did. To 70 cc. of nitric acid (sp. gr. 1.42) add 50 g. of *powdered* tartaric acid, and stir well. Add conc. sulfuric acid (sp. gr. 1.83) slowly, with stirring, until the tartaric acid is all dissolved; then add the balance of the sulfuric acid (200 to 250 cc. in all). Allow the mixture to cool slowly for several hours. Filter off the excess of sulfuric acid on a Büchner funnel; ordinary filter paper may be used if moderate suction is applied. Stir the cake with about 300 g. of ice until all lumps are broken up, and extract the mixture with ether. Wash the ether twice with small amounts of ice-water, and dry with calcium chloride for a short time. Evaporate the ether carefully on the water-bath until brown fumes begin to appear, then allow to evaporate spontaneously. The product, except for traces of water and dihydroxy-tartaric acid, is practically pure nitrotartaric acid. The yield is from 60 to 75%.

Properties.—Nitrotartaric acid crystallizes in soft, white needles

which interlace much like those of asbestos. It is quite soluble in water, very soluble in alcohol, amyl alcohol, acetone, ether; insoluble in ligroin, benzene, etc. If carefully dehydrated over lime or caustic soda, it seems to keep indefinitely in a perfectly dry atmosphere. As ordinarily obtained, it smells of nitrous acid; the perfectly dry acid is odorless. For analysis, the acid was dissolved in dry ether, and precipitated by benzene.

Alkalies act violently on nitrotartaric acid, even in very dilute or in alcoholic solution, with practically complete decomposition, as discussed below. It is, however, unexpectedly stable towards sodium carbonate, and on titration shows itself to be a dibasic acid.

Subs., 0.2949 : 0.1 *N* sodium carbonate sol., 24.8 cc. (Equivalent to 100.6% nitrotartaric acid.)

Working at 0°, a perfectly sharp end-point is obtained with methyl orange as indicator.

The strength of nitrotartaric acid is manifested by its action on calcium chloride when the latter is used to dry its ethereal solution. After several hours, the calcium chloride lumps are covered with a feathery mass, which after 2 days fills the entire liquid; the ether then contains nitrosyl chloride. The solid consists of a mixture of the calcium salts of nitrotartaric and dihydroxy-tartaric acids.

On careful evaporation of a concentrated solution of nitrotartaric acid in sodium carbonate, a solid sodium salt can be obtained, though in impure form. This salt, although extremely soluble, is not deliquescent. It seems to show an abnormal behavior, which is still under investigation.

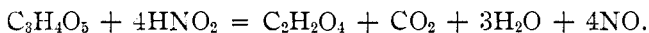
Moist nitrotartaric acid decomposes with some violence well below 100°; the perfectly dry substance, however, was heated in xylene to the boiling point of the latter, without change.

When solutions of nitrotartaric acid in water are allowed to stand, they soon turn blue, gases are given off, and much heat is evolved. If the temperature is kept under control by water cooling, the process lasts from one to two days. The gases consist at first of nitrogen trioxide; later they become colorless, and are composed of nitric oxide and carbon dioxide. The solution contains chiefly dihydroxy-tartaric acid, which may be precipitated by addition of sodium acetate or carbonate as the very insoluble sodium dihydroxy-tartrate; it also contains tartronic and oxalic acids. The yield of sodium dihydroxy-tartrate is from 75 to 80%.

Little or no *tartaric* acid is formed; the highest amount found in many different hydrolyses was 1.3% of the possible yield; in a few cases, its presence could not be shown by the Goldenberg method.

The formation of tartronic acid during the above-described hydrolysis is due to the decomposition of dihydroxy-tartaric acid, as shown previously by Kekule and by Gruber; the latter acid loses carbon dioxide and passes over into tartronic acid. The mechanism of this reaction is

not clear, and it is now being investigated. The production of oxalic acid is due to a side reaction, *viz.*, the oxidation of tartronic acid by nitrous acid,



This was proved by slowly adding a solution of tartronic acid to sodium nitrite; a copious precipitate of sodium oxalate was obtained. Tartaric and dihydroxy-tartaric acids, treated similarly, gave no oxalic acid whatever.

The Action of Alkalies on Nitrotartaric Acid.

When nitrotartaric acid is neutralized with caustic soda, the action is accompanied by the immediate evolution of considerable heat. Regardless of dilution within ordinary limits, cooling to -5° , or use of alcohol as a solvent, the same results are obtained, *viz.*, production of sodium nitrite in practically quantitative yield, and complete decomposition of the dihydroxy-tartaric acid. It is not necessary to give the experimental details of the numerous experiments that were made. Entirely similar results were noted when calcium hydroxide was employed. In place of dihydroxy-tartaric acid are found tartronic acid, as already noted by Skinner,¹ and a considerable amount of oxalic acid. The latter probably owes its formation to intramolecular condensation of diketosuccinic acid, with simultaneous formation of glyoxalic acid.

$\text{COOH} - \text{CO} - \text{CO} - \text{COOH} + \text{H}_2\text{O} = \text{COOH} - \text{COOH} + \text{CHO} - \text{COOH}.$
This reaction is now being studied.

The identification and separation of mixtures of the various acids encountered is a difficult and tedious matter; tartronic and oxalic acids are particularly hard to separate quantitatively.

Discussion of Experimental Results.

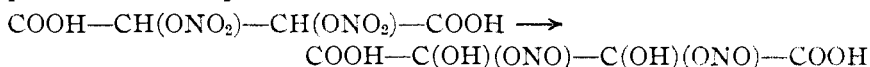
It has been shown that in the solid form, in the presence of strong acids, nitrotartaric acid is a true *nitrate* of tartaric acid. In aqueous solution, however, and when acted upon by alkalies, it behaves like a nitrite of dihydroxy-tartaric acid. The yield of dihydroxy-tartaric acid in the aqueous hydrolysis is good, considering the ease with which that acid is decomposed; and the yield of nitrous acid on hydrolyzing with alkalies is almost quantitative. Nef,² a number of years ago, showed that nitric esters of both fatty and aromatic alcohols yield considerable amounts of nitrous acid when saponified with alcoholic alkalies; the experimental conditions involved rather high concentrations of alkali, and the practical absence of water. In the present instance, the same reaction occurs in the complete absence of alkali, and in the presence of water. It may be taken for granted that the mechanism of the reaction is the same in both

¹ Skinner, *J. Chem. Soc.*, **73**, 488 (1898).

² Nef, *Ann.*, **309**, 175 (1899).

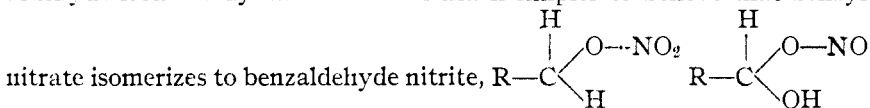
cases; nitrotartaric acid is an aggregation of strongly electro-negative components; benzyl nitrate becomes more electro-negative under the influence of alkali.

The best explanation of the behavior of nitrotartaric acid is that it passes over into a pseudo form as follows:



This would appear to be a new type of tautomerism, involving the shifting of an oxygen atom instead of a hydrogen atom. The possibility of an hydroxyl group attached to nitrogen is excluded by the fact that nitrotartaric acid is only *dibasic*; such a combination would almost certainly be strongly acid.

The suggested explanation of the formation of nitrous acid and a ketone, in the case of nitrotartaric acid, seems less forced than Nef's assumption of a "methylene dissociation" in the formation of nitrous acid and benzaldehyde from benzyl nitrate. It is much simpler to believe that benzyl



which then loses NO—OH .

Nitroglycerine, like nitrotartaric acid, contains an accumulation of negative groups, and is therefore also sensitive to traces of acids, yielding nitrous acid and more or less complex aldehydes as first products, with rapidly increasing evolution of energy.

Owing to the comparative stability of dihydroxy-tartaric acid, it is possible to isolate it as the first product in the progressive decomposition of a nitric ester, and thus gain a clearer insight into the nature of explosive processes in general.

Summary.

1. Nitrotartaric acid is shown to be a true nitric ester of tartaric acid.
2. The decomposition of nitrotartaric acid in aqueous and in alkaline solution has been studied. The acid behaves as if it were the nitrous ester of dihydroxy-tartaric acid.
3. Nitrotartaric acid probably exists in 2 tautomeric forms, characterized by the shifting of an oxygen atom.
4. The decomposition of other nitric esters, such as nitroglycerin, is analogous to the behavior of nitrotartaric acid.