

by T.L.C. and filter-paper chromatography and via the oxalate of ephedrine.

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ESTIMATION OF NITRATE IN PHOSPHORIC ACID

THE presence of nitrate in different phosphates is encountered in mixed fertilizers, animal foods, phosphate complexes used in drugs and medicines. In the latter cases the presence of nitrate is highly undesirable due to the fact that nitrate gets reduced to the poisonous nitrite in the intestine. Since phosphoric acid is the starting material for many of the phosphates used in medicine, it has been felt necessary to develop a satisfactory method for detection and estimation of nitrate in phosphoric acid.

During the investigation on the instability of permanganate in orthophosphoric acid, it has been observed that Mn(III) is formed as a brown solution¹, which turns violet in presence of Mn(II). It has, now, been observed that the same coloured complex is produced in orthophosphoric acid when Mn(II) is oxidised by nitrate. The nitrate, in turn, gets reduced to nitrite. The reaction takes place in presence of a reagent like urea or sulphamic acid, that is capable of removing nitrite as nitrogen. Mn(III) thus formed may be estimated titrimetrically or colorimetrically, the concentration of which is directly proportional to the nitrate present in the solution. It has been observed that this reaction can be used as a qualitative test for nitrate present in phosphates or phosphoric acid or otherwise.

It has been reported that Mn(III) solution in phosphoric acid has a strong absorption in UV which tails off into the visible region, with a shoulder around 510 m μ . When small amount of Mn(II) is added, absorbance in the 350–450 m μ region decreases and the shoulder around 510 m μ appears as a peak (Fig. 1, curve II). As more Mn(II) is added, the band at 510 m μ gains more intensity (curve III). The colour of such a solu-

tion resembles that of permanganate visually; the absorption spectra are, however, entirely different. The spectrum of the violet coloured solution obtained by the nitrate oxidation of Mn(II) is superimposable on curve III of Fig. 1. This is a clear indication for the fact that the oxidation product is Mn(III). Purple or violet coloured Mn(III) solutions in acid media have been reported in literature²⁻⁵. Meyer and Marek² have observed that the compound $\text{H}_3\text{Mn}(\text{PO}_4)_2$ is formed in phosphoric acid solutions from which salts like $\text{Na}_2\text{HMn}(\text{PO}_4)_2$ can be isolated. Extending this idea, the formation of violet complex, in the present case, may be due to $\text{Mn(II) HMn(III)(PO}_4)_2$.

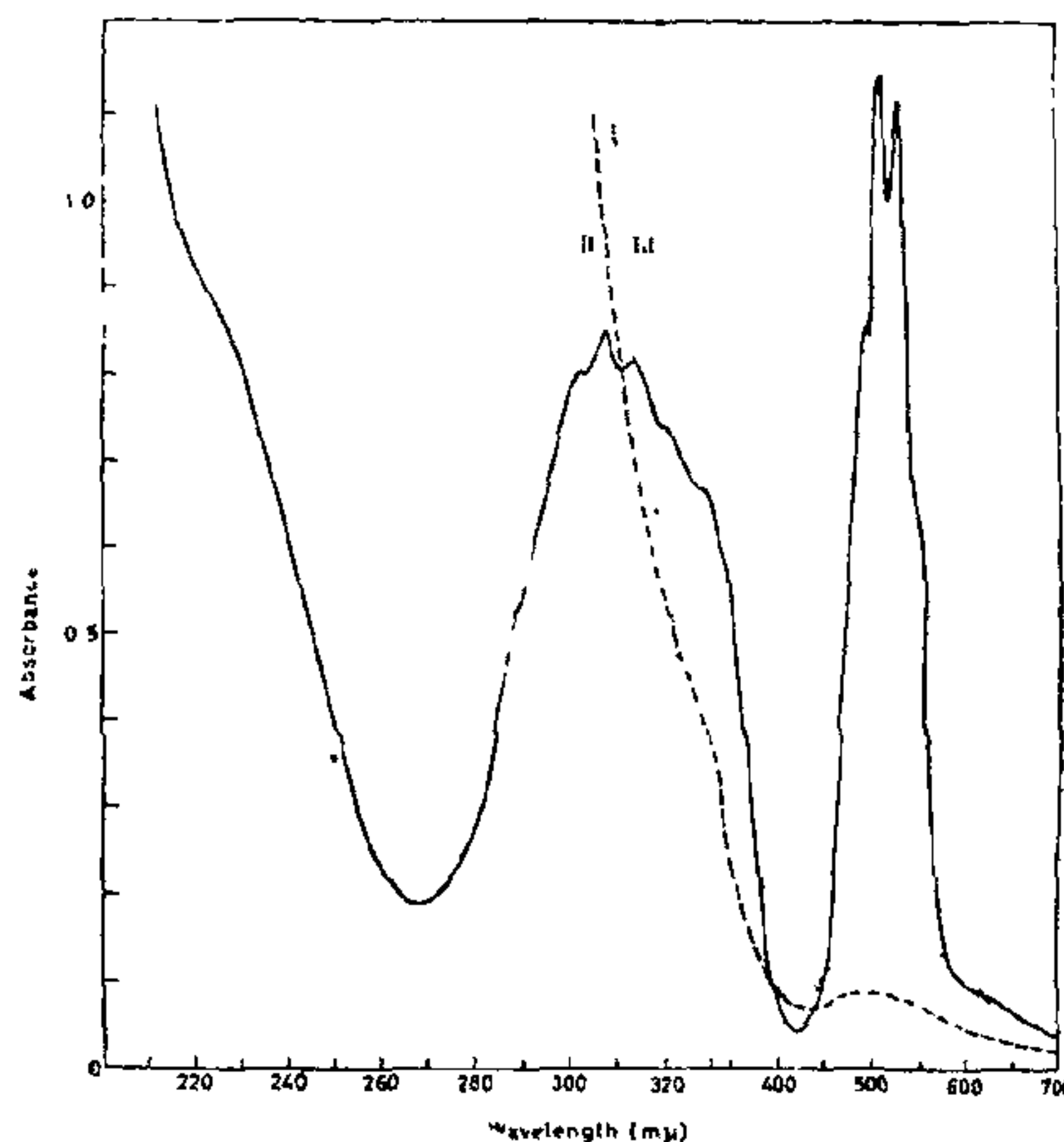


FIG. 1. Electronic absorption spectra: I. KMnO_4 in H_2O ($0.5 \times 10^{-3} \text{ M}$); II, Mn(III) in H_3PO_4 ; III, Mn(III) in presence of Mn(II) in H_3PO_4 from NO_3^- oxidation.

In typical experiments, 50 to 100 mg of potassium or sodium nitrate is dissolved in 15 ml of 88% H_3PO_4 . Alternatively, if 100% acid is used, the nitrate is dissolved in minimum amount of water such that the net concentration of the solution is 88% with respect to H_3PO_4 . The solution is warmed to 60° C and 0.6 to 0.8 gm of manganous carbonate [free of Mn(III)] is dissolved in the same. The solution is kept on a boiling water-bath for 10 minutes. The resulting solution has a faint violet colour. If urea is added (50 mg) to the mixture prior to the addition of manganous carbonate, the violet manganese(III) complex produced is quite considerable. The same results are obtained when urea nitrate, $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$, is used instead of alkali nitrate and urea separately. The manganese(III) compound thus formed is

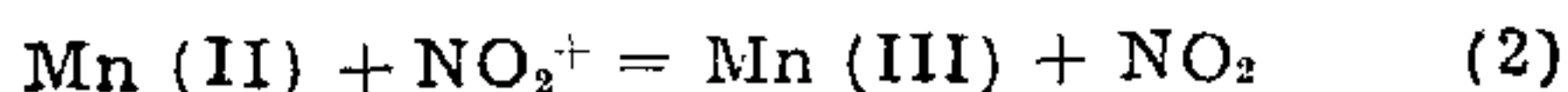
estimated titrimetrically using standard ferrous sulphate or iodometrically using starch as the indicator, after diluting the solution. Alternatively, the manganese(III) complex is found to obey Beer-Lambert law at 510 m μ when increased amount of nitrate is employed. It has been found that nearly two equivalents of Mn(III) are produced per mole of nitrate. This supports the fact that nitrite or nitrogen(III) oxides are the reaction product.

The role of urea is to remove the lower oxides of nitrogen as well as nitrite formed as mentioned above. When urea is replaced by sulphamic acid, NH₂SO₃H, the results are found to be the same. However, longer time of heating or bringing the solution to boiling is necessary in the latter case. For the same reason, the results are found to be not quantitative with sulphamic acid. A reverse estimation, i.e., by taking excess nitrate and smaller amount of manganous compound, is found to be not quantitative. This can be expected due to the incomplete removal of nitrite.

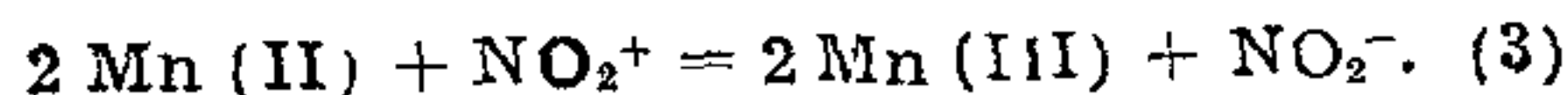
The chemical nature of nitrate or nitric acid in strong acids is connected with the formation of nitronium ion, NO₂⁺. The origin of NO₂⁺ is explained to be due to the ionisation of the type:



NO₂⁺ thus formed can be involved in an electron transfer reaction as:



or



This may result in the formation of the coloured manganese(III) complex in phosphoric acid.

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SYNTHESIS AND BACTERIOSTATIC ACTIVITY OF LINEAR (7, 6) AND ANGULAR (7, 8)- α -PYRONOCHROMONES

INVESTIGATIONS carried out by several groups of workers in oxygen heterocycles have revealed that both benzo α -pyrone and benzo γ -pyrone moieties are inherently physiologically active, and suitable substituents enhanced their activity. It is this consideration that has prompted us to build condensed ring systems containing α -pyrone as well as γ -pyrone rings with a view to examine their physiological activity. In continuation of our earlier work on α -pyronoisoflavones¹ we now report the synthesis and bacteriostatic activity of a number of 7, 6- and 7, 8- α -pyronochromones.

In the present work linear (7, 6)- α -pyronochromones have been synthesized by building a γ -pyrone over an α -pyrone moiety whereas angular (7, 8)- α -pyronochromones have been synthesised by building either a γ -pyrone over a coumarin or by building an α -pyrone over a chromone.

4-Methyl-6-propionyl-7-hydroxy coumarin and 4-methyl-6-phenylacetyl-7-hydroxy coumarin¹ when subjected to Kostanecki reaction with sodium acetate, acetic anhydride and sodium propionate and propionic anhydride yielded the 2-methyl and 2-ethyl α -pyronochromones respectively. These 0-hydroxy acyl coumarins when condensed with various aryl chlorides like benzoyl veratroyl piperminoyl, trimethyl galloyl and *p*-nitrobenzoyl chlorides in the presence of potassium carbonate in refluxing acetone yielded the corresponding 2-aryl- α -pyronochromones, in a single step, in very good yields. The compounds prepared along with their analytical data are presented in Table I.

Similarly 5-hydroxy-6-propionyl-4-methyl coumarin and 4-methyl-6-phenylacetyl-5-hydroxy coumarin² when subjected to Kostanecki reaction and Baker-Venkataraman reaction with same acid chlorides yielded the corresponding 2-alkyl and 2-aryl-7, 8- α -pyronochromones in excellent yields. The compounds prepared along with their analytical data are listed in Table II.

2, 3-Dimethyl-7-hydroxy-8-formyl, 2-phenyl-3-methyl-7-hydroxy-8-formyl³, 2(4'-nitro) phenyl-3-methyl-7-hydroxy-8-formyl and 2-methyl-3-phenyl-7-hydroxy-8-formyl chromones⁴ when subjected to Perkin reaction with sodium acetate, acetic anhydride and sodium propionate, propionic anhydride yielded the corresponding α -unsubstituted and α -methyl substituted α -pyronochromones in good yields. Table III contains the M.P. and analytical data of angular (7, 8)- α -pyronochromones synthesised by this procedure.