

Determination of sugar acids and related compounds by vanadium(V) in perchloric acid : The product analysis and probable mechanism of oxidation

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A mixture of the reductant and an excess of Na(or NH₄)VO₃ in dilute HClO₄ has been slowly refluxed for 40 min and the residual metavanadate determined iodometrically. The metavanadate has been standardised against either Na₂S₂O₃ or the respective reductant of known strength for better results. The product analysis, the probable reaction mechanism, the methods for removal of interferants and the detection of adulterants in aldoses have been reported.

Vanadium(V) in perchloric acid had been used to determine glucose¹ and other mono- and di-saccharides² in this laboratory. Recently Pfaffenberger³ mentioned different methodologies and clinical aspects of the analysis of sugars and related compounds. Periodic acid⁴ and permanganate^{5,6} have been used for the oxidation of α -hydroxy acids. Various physical and physicochemical techniques such as colourimetry⁷, spectrophotometry⁸, polarimetry⁹, gas chromatography¹⁰, thin layer chromatography¹¹ and gas liquid chromatography¹² have been reported. Other interesting methods include iodometric method¹³, separation of sugars using resins¹⁴ and photochemical oxidation with Ce(IV)¹⁵. It has been envisaged that determination of a few hydroxy acids and sugar acids like galactonic, gluconic, glucuronic and saccharic acids and simultaneous product analysis could be helpful for proposing the probable mechanism of oxidation of sugar and sugar acids. Hence the present work was undertaken.

Experimental

D-Glucuronic acid, hemicalcium salts of D-gluconic and D-galactonic acids, and calcium salt of D-saccharic acid (all of Sigma) were dried in vacuum before use. Other reagents were of guaranteed reagent grade. Freshly prepared starch solution was used as indicator and doubly distilled

water (prepared by refluxing over KMnO₄) was used throughout.

A solution of Na (or NH₄)VO₃ (0.05 mol) in hot water (200 ml) was slowly added to cold HClO₄ (70 %; 170 ml) in water (200 ml) and standardised against standard solution of either Na₂S₂O₃ or the organic reductant which was to be analysed as the unknown sample.

A mixture of organic sample (0.1 mmol approx., as solid or in solution) and an excess of standard metavanadate solution contained in a standard jointed (B-24) flask was slowly refluxed for 40 min. The condenser was washed down with water (not exceeding 10 ml) into the cold green-blue reaction mixture and the residual metavanadate was determined iodometrically. Blank experiments were performed during the determination of organic sample present as unknown one either in the solution or as solid sample. In this way oxalic, tartaric, citric, glucuronic acids and hemicalcium salts of gluconic and galactonic acids were determined, the errors were within ± 0.5 %, but with calcium salt of saccharic acid, the error was between -5.00 and $+0.26$ %.

The steam distilled product of the reaction mixture responded strongly to the test of formic acid with HgCl₂ (ref. 16) but it did not furnish 2,4-D.N.P. derivative as well as colour reaction with chromotropic acid thus confirming the absence of formaldehyde in the distillate. The aforementioned formic acid generated in the reaction mixture from the organic compounds followed by steam distillation was collected directly in the standard NaOH solution for quantitative estimation of formic acid. Experiments with authentic formic acid revealed that it consumed vanadate very slowly under the experimental condition.

Determination of CO₂ (if formed in the reaction mixture) was carried out in the following way. The three necked reaction flask containing vanadate was fitted with an upright condenser which was connected to two consecutive H₂SO₄ wash bottles. A stream of N₂ (passed through NaOH solution) was bubbled through the boiling vanadate solution for 15 min to remove CO₂ already present in the system. Then two U-tubes each containing "carbosorb" soda asbestos (10-14 mesh; 63 % Na₂O, BDH) were connected in the series to the outlet of the aforementioned H₂SO₄ wash bottles, dipping the free end of the second U-tube through a glass tube into H₂SO₄. Then the substrate was added, the reaction mixture boiled

Table 1—No. of moles of CO₂ and HCO₂H formed and comparative study of the vanadate requirement for various substrates during oxidation with vanadium(V) and equations of the reactions

| Name of the substrate [Molecular weight] Approx. moles of CO ₂ ; (Approx. moles of HCO ₂ H) | No. of moles of V(V) consu- med per mole substrate (expt. value) | Proposed reaction HCOOH = A; CO ₂ = B; H ₂ O = C; VO ⁺⁺ = D | Equivalent weight of reductant E |
|--|--|--|---|
| Glucose [180] negligible, (5.8 ≈ 6) | 12 (12.04) | C ₆ H ₁₂ O ₆ + 12H ⁺ + 12VO ₂ ⁺ → 6A + 6C + 12D | [15] |
| Fructose [180] 1 (4.85 ≈ 5) | 14 (13.88) | C ₆ H ₁₂ O ₆ + 14H ⁺ + 14VO ₂ ⁺ → 5A + B + C + 14D | [12.85] |
| Arabinose [150] negligible, (4.74 ≈ 5) | 10 (9.93) | C ₅ H ₁₀ O ₅ + 10H ⁺ + 10VO ₂ ⁺ → 5A + 5C + 10D | [15] |
| Oxalic acid [126] (dihydrate) | 2 (2.01) | C ₂ H ₂ O ₄ .2H ₂ O + 2H ⁺ + 2VO ₂ ⁺ → 2B + 4C + 2D | [63] |
| Citric acid [192] | 2 (1.80) | C ₆ H ₈ O ₇ + 2H ⁺ + 2VO ₂ ⁺ → CH ₃ COCH ₃ + 3B + 2C + 2D | [96] |
| Tartaric acid [150] | 6 (5.90) | C ₄ H ₆ O ₆ + 6H ⁺ + 6VO ₂ ⁺ → 2B + 2A + 4C + 6D | [25] |
| Calcium salt of saccharic acid [248] 2, (3.65 ≈ 4) | 10 (9.85) | Ca C ₆ H ₈ O ₈ + 12H ⁺ + 10VO ₂ ⁺ → 2B + 4A + 6C + 10D + Ca ⁺⁺ [24.8] | |
| Glucuronic acid [194], 1 (4.65 ≈ 5) | 10 (9.59) | C ₆ H ₁₀ O ₇ + 10H ⁺ + 10VO ₂ ⁺ → B + 5A + 10D + 5C | [19.4] |
| Hemicalcium salt of gluco- nic acid [215], 1 (4.53 ≈ 5) | 12 (11.65) | (C ₆ H ₁₁ O ₇) ₂ .Ca + 26H ⁺ + 24VO ₂ ⁺ → 10A + 2B + 14C + 24D + Ca ⁺⁺ [17.9] | |
| Hemicalcium salt of galactonic acid [215], 1 (4.52 ≈ 5) | 12 (11.76) | (C ₆ H ₁₁ O ₇) ₂ .Ca + 26H ⁺ + 24VO ₂ ⁺ → 10A + 2B + 14C + 24D + Ca ⁺⁺ [17.9] | |

(i) Formation of acetone was confirmed through 2,4-DNP derivative and iodoform. (ii) Aldoses did not furnish CO₂. (iii) Formaldehyde was never obtained. (iv) Each experiment was repeated many times.

(40-50 min) and CO₂ formed was calculated from the observed increase in weights of the U-tubes. The blank experiments were always done. Iodometric determination of the residual vanadate indicated the vanadate equivalent of the reductant (Table 1).

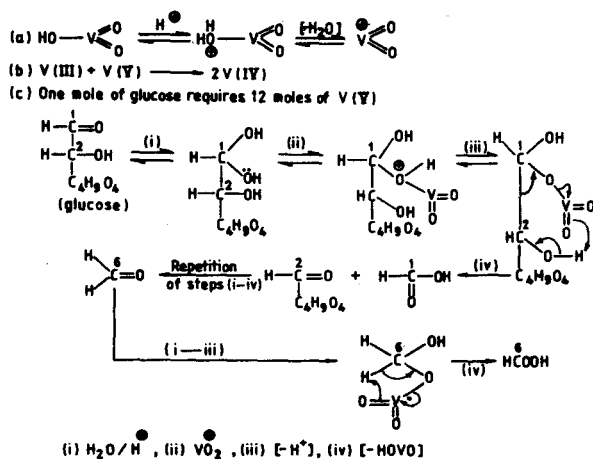
Results and discussion

It was observed that oxalic and aliphatic hydroxy acids were completely consumed by vanadate within 20 min. but alkanolic and alkanedioic acids remained totally unaffected. Since HCO₂H was slowly consumed by vanadium(V) solution coupled with its exponential distillation, its quantitative recovery was not possible. Hence the amount of HCO₂H collected by steam distillation never exceeded 95% of its theoretical value (Table 1).

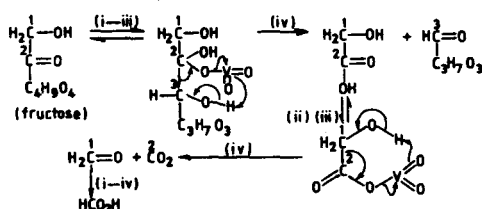
The stoichiometry proposed for each sample fitted well with the experimental results. Aldoses, C_nH_{2n}O_n, gave n moles of HCO₂H only, involving

2n electron-transfer processes. But fructose gave one mole of CO₂ and five moles of HCO₂H requiring fourteen electron transfer process. Each -COOH group present in the hydroxy acids yielded one mole of CO₂ (Table 1).

A mechanism, which is new and different from that of Rizvi and Singh¹⁷ and consistent with the derived products and calculated vanadate equivalent, is proposed in Scheme 1 for the oxidation of sugars and related carboxylic acids. A vanadate complex is formed in the transition state which undergoes fast decomposition to yield CO₂ and/or HCO₂H and a new product substrate which reacts with fresh oxidant. In all probability vanadium(V) initially comes down to vanadium(III), the latter undergoes disproportionation with vanadium(V) to furnish vanadium(IV)¹⁸. Scheme 1 explains the final products formed but it involves the intermediate formation of H₂CO (from the primary alcoholic



One mole of fructose requires 14 moles of V(V)



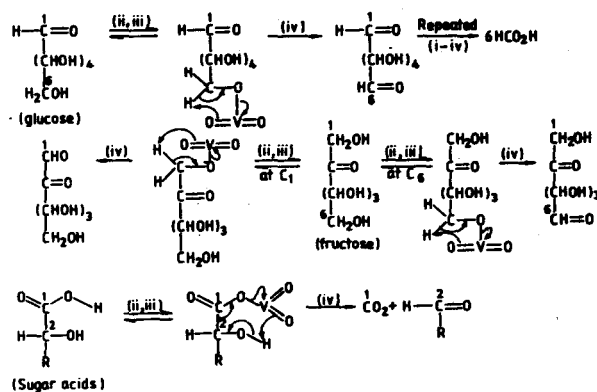
Scheme 1

group) which must have been isolated and identified by steam distillation during product analysis. But H_2CO was never obtained. Hence Scheme 2 is proposed which involves the formation of vanadate complex by the initial attack of VO_2^+ on the sterically favoured primary alcoholic group followed by its decomposition into carbonyl group thereby avoiding the generation of H_2CO during the vanadate oxidation of sugars.

Applications

Removal of water, insoluble interferants was effected by filtration. Sparingly soluble interferants could be removed by extraction with pure and freshly distilled chloroform or benzene or ether. Chloroform extraction was more convenient and it did not affect the determination of sugars contained in the aqueous solution. Water soluble steam volatile interferants were removed by repeated evaporation of the solution to dryness on a steam bath followed by determination of sugars.

Detection of adulterants (generating CO_2 during oxidation) in aldoses was possible by steam distillation of the reaction product and collecting the distillate directly into freshly prepared lime water which turned milky. Thus sucrose, fructose, sugar acids (gluconic etc.), aliphatic hydroxy acids (tartaric etc.) and oxalic acid when present (as low as 30 mg) in aldoses (glucose, arabinose etc.) was readily detected by this method.



Scheme 2

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