

difficulty has been overcome by using acetone as the bromine scavenger. But salicylaldehyde and vanillin could not be oxidised to the corresponding acids under similar experimental condition showing that phenolic aldehydes are unsuitable for bromate oxidation. Cinnamaldehyde produced cinnamic acid in moderate yield indicating that the double bond remained unaffected by bromate. Citral, on the other hand, failed to produce the desired acid and butyraldehyde furnished impure butyric acid. Bromine was evolved in each case. It appeared that aliphatic aldehydes were difficult to oxidise. It was also observed that the use of dilute sulphuric acid during the bromate oxidation of substituted benzaldehydes holding ring-activators favoured the introduction of bromine atom in the ring in a regioselective manner, the electron attracting groups accelerated the rate of oxidation while the electron releasing groups retarded it. From the kinetic study² carried out in dilute acetic acid solution, it has been found that the rate of oxidation of the aldehyde at temperature ranging from 40 to 60° is dependent on the substrate and acetic acid but not on the oxidant. The oxidation of other classes of organic compounds is under investigation.

Experimental¹

General procedure: A mixture of weighed amount of substituted benzaldehyde and half its weight of potassium bromate in acetic acid (15 ml per g of starting aldehyde) was heated under reflux for 15 min. Bromine evolved which escaped the reaction mixture. The latter was cooled, poured onto water, saturated with sodium chloride and extracted thrice with chloroform. The organic layer was extracted with saturated sodium bicarbonate solution, washed with water and dried over anhydrous sodium sulphate. On removal of the solvent no starting material was obtained excepting cinnamaldehyde, salicylaldehyde and citral. The alkaline extract was acidified with dilute sulphuric acid (congo red) and the precipitated organic acid was extracted thoroughly with either chloroform or ether. The organic layer was washed with small amount of water, dried and the solvent removed to furnish the desired acids which were crystallised, if required, for further purification. The results are presented in the order: derived acid (% yield), melting point[°], spectral data and/or other supporting evidence and [Remarks if any]. The IR spectra were taken in Perkin-Elmer Model 597 Infrared grating spectrophotometer. The m.m.p. of each solid product with authentic specimen remained undepressed. (a) 2-Nitrobenzoic acid (95%), 142°^{sa}. (b) 3-Nitrobenzoic acid (99%), 136°^{sa}, N.E. 165 ± 5 [no bromination during oxidation if 4 N sulphuric acid is used]. (c) 4-Nitrobenzoic acid (99%), 241°^{sb}. (d) 2-Chlorobenzoic acid (90%), 137°^{sa}. (e) 3-Chlorobenzoic acid (85%), 157°^{sa}, N.E. 152 ± 5. (f) 4-Chlorobenzoic acid (90%), 237°^{sa}. (g) 2-Methoxybenzoic acid (72%), 101°^{sa}, ν_{max}^{KBr} 1690, 1610, 1590, 1470, 1430, 1310, 1295, 1230, 1045, 935, 910, 805 and 760 cm⁻¹; N.E. 150 ± 5, [5 ml of acetone was used per g of 2-methoxybenzaldehyde

during oxidation, otherwise brominated product, m.p. 120-135° was obtained]. (h) 3-Methoxybenzoic acid (55%), 105-107°^{sa}, ν_{max}^{KBr} 1693, 1607, 1586, 1462, 1379, 1310, 1291, 1230, 1121, 1105, 1089, 1043, 936, 908, 891, 869, 810, 755, 679 and 665 cm⁻¹; [acetone was used during oxidation as in (g)]. (i) 4-Methoxybenzoic acid (90%), 182°^{sf}, ν_{max}^{KBr} 1680, 1605, 1580, 1515, 1425, 1305, 1260, 1180, 1170, 1132, 1108, 1025, 925, 895, 825, 775, 698, 635, 615, 605 and 540 cm⁻¹; N.E. 151 ± 5, [mineral acid induced bromination during oxidation]. (j) Cinnamic acid (40%), 131°^{sg} [recovered cinnamaldehyde, 55%, b.p. 210-220°]. (k) Butyric acid (55%), b.p. 130-140°/water aspirator [contained traces of bromo-compound].

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Potentiometric Determination of Niobium(V) in Presence of Tantalum in Non-Aqueous Media¹

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NIObium salts hydrolyse easily in aqueous media and their direct estimation in such media presents some difficulty. Many niobium compounds are soluble in non-aqueous media but their estimation by usual methods takes time. Estimation of niobium or tantalum in the presence of each other is also considered difficult.

Bismuth has been estimated using 5-mercapto-3-phenyl-1,2-thio-1,3,4-thio-diazolone-2-phenylidithio-diazolone (MPTTPT) in acid medium when a reddish-coloured precipitate is obtained. Bismuth has also been detected and estimated colorimetrically using this reagent. The reagent also forms yellow precipitates with gold, mercury, lead, silver, platinum, arsenic and antimony; white with cadmium, zinc; brown with copper; brick red with tin and red with palladium^{1,2}.

The authors earlier reported the gravimetric estimation of niobium using the reagent in aqueous media⁸. No reference has been found in literature regarding the use of this reagent in electrometric methods.

Experimental

E.M.F. measurements were made with a digital pH meter (ECL Model PH 5651) having a single glass-calomel electrode assembly.

Preparation of niobium solution: Requisite quantity of niobium pentachloride (Fluka) was dissolved in absolute alcohol. Care was taken to avoid moisture while weighing.

Preparation of the reagent: The reagent was prepared by the described method⁴. The compound is fine white needles, m. p. 259° and is soluble in water and warm alcohol.

MPTTPT was dissolved in slightly warm absolute alcohol. The strength of the reagent solution was kept the same as that of the niobium pentachloride solution.

5 ml of niobium pentachloride solution was taken in the cell every time and the titrant (MPTTPT reagent) solution added from a microburette. Direct and reverse titrations were performed. Several such experiments were performed using 0.01M, 0.005M and 0.004M solutions of niobium pentachloride. In all the titrations, sharp change was noticed at the equivalence point after which the potential became steady again. The end-point was obtained from the maximum of $\Delta E/\Delta V$ and corresponds to 1:1 complex.

It is noteworthy that tantalum does not interfere in the estimation of niobium by this method. The method described above is rapid and accurate for the estimation of such compounds of niobium which get hydrolysed in aqueous media but are soluble in absolute alcohol.

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Determination of Equilibrium Constant of Ferric Formate Complex by Paper Electrophoresis

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PAPER electrophoresis has been applied to the study of metal complexes in solution. Attempts have also been made to determine the stability constants of the complex species¹⁻¹⁰.

As far as we are aware the stability constant has not been determined from the eluate of the cationic and anionic species of the migrant obtained after paper electrophoresis. In the present study, an attempt has been made to determine the equilibrium constant of the Fe(III)-formate system by paper electrophoresis.

Experimental

Preparation of migrant solution: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.0100 g) was dissolved in 30 ml water with addition of a few drops of hydrochloric acid. The solution was filtered and the volume made up to 50 ml.

Preparation of the background electrolyte: Stock solutions of 2M formic acid, 2M sodium formate and 1M sodium nitrate were prepared. The background electrolyte consisted of a mixture containing 25 ml 2M sodium formate, 25 ml 2M formic acid and 50 ml 1M sodium nitrate per 100 ml solution. Sodium nitrate was used to attain the desired ionic strength. Formate concentration was fixed, ionic strength was 1.0 and the pH of the electrolyte was 3.75.

Instrument: Wieland and Fischer type horizontal set was used¹¹. The apparatus used was the cassette type and chromatograms could be run simultaneously on six paper strips. High voltage electrophoresis was carried out for 20 min at 400 volts and at 30°. Whatman No. 1 paper strips (3 × 40 cm) were used with an applied voltage gradient of 8 volt/cm.

pH measurements were made with an Elico Model L1-10 pH meter using a glass-calomel electrode assembly.

Procedure: The midpoint of each paper strip was marked and moistened with the background electrolyte and a spot of the metal solution was applied on it. The electrophoretic migration of the metal spots of different volume on the paper was observed. After electrophoresis, the spots of Fe(III) were developed with yellow ammonium sulphide. Two species were obtained in each case, one moved towards the anode and the other towards the cathode. The distances of the leading and tailing edges of the spots from the marked centre were measured. Portions of the paper containing the ions were cut out from the dried undeveloped electrophoregram after matching the positions of the ions with a developed electrophoregram subjected to identical electrophoretic conditions and environment. The paper portions containing the ions were treated with 0.8 N H_2SO_4 , to extract the ion. The extracts derived out of the strips through washings were taken in a 25 ml volumetric flask and the volume made upto the mark with 0.8 N H_2SO_4 . Similarly, blank solutions were prepared. The absorbance of the eluted iron solution was measured against these blanks at 305 m μ (Table 1).

In both the anionic and cationic species the metal ion Fe(III) present in each case was calculated