OXIDATION OF SODIUM (2-14C) ACETATE WITH ALKALINE PERMANGANATE

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The mechanism and kinetics of the oxidation of sodium acetate with permanganate in alkaline and neutral media, has been investigated using (2-14C) acetate. The reaction is first order both with respect to permanganate and acetate ions. The initial second order rate constants depend linearly on the square of the hydroxide ion concentration. Arrhenius activation energy of the oxidation reaction carried out in 12M NaOH is 24.0 kcal/mole in the temperature interval 50–100 °C. The mechanism of the principal path leading to the oxalate formation and the mechanism of the side reaction resulting in the carbon dioxide production has been proposed and discussed.

Introduction

So far the mechanism and kinetics of oxidation of isotopically labelled formic and propionic acids with permanganate have been investigated quite thoroughly.1–7 In this communication kinetic parameters characterizing the oxidation of fairly inert sodium acetate, the second one in the series of aliphatic fatty acids, with alkaline permanganate8,9 are reported.

Experimental

(2-14C) Acetic acid, diluted with acetic acid p.a. of natural isotopic composition to the specific radioactivity suitable for internal gas phase counting was purified by fractional semimicro distillation. Reaction vessels closed with a pair of standard vacuum joints and stopcocks were charged in carbon dioxide free atmosphere of the radiochemical box with the required quantities of sodium (2-14C) acetate obtained in situ, sodium hydroxide p.a., permanganate p.a. and placed after vigorous shaking until homogeneous in the ultrathermostat. The vacuum stopcock was closed a few seconds after immersion of the vessel into the thermostat to avoid excess pressure. Reaction times and concentrations of the substrates are given in column 1–4 of the Tables 1–3. The total volume of the solution at room temperature was 10 cm³. The course of the oxidation
was stopped by freezing the postreaction mixture with liquid nitrogen. Then two analytical procedures were applied. At relatively large degrees of oxidation the frozen compounds of the manganese (VI) were reduced to MnO₂ with 3% H₂O₂. Manganese dioxide was separated from the rest of the postreaction solution by high speed centrifugation and washed several times with distilled water. The alkaline postreaction solution free of MnO₂ was transferred to the vacuum reactor, connected with the vacuum line, and treated with an excess of diluted acetic acid. After fast extraction of ¹⁴CO₂ evolved by evacuating and freezing it in the series of vacuum traps immersed in liquid nitrogen the solution remaining in the reactor was transferred to the crystallizer, the oxalate precipitated by dropwise addition of calcium acetate solution and separated after 12 hrs of room temperature slow crystallization. After several washings with water, then with ethanol the calcium oxalate was dried, weighed and radioassayed by the internal gas filling method. The specific radioactivity of oxalate obtained at partial oxidation of (2-¹⁴C) acetate was slightly lower than the specific radioactivity of oxalate obtained at complete oxidation of acetate with alkaline permanganate indicating the small K.I.E. for ¹⁴C in the oxidation reaction studied, corresponding to the C – H bond rupture. The total volume of the ¹⁴CO₂ extracted from carbonates by acidifying the free of MnO₂ postreaction solution with acetic acid and its radioactivity measurements were used to determine the correct amount of carbonates formed in the side reaction path in the course of the oxidation of acetate. The 10–12% yield of carbonates has been reached when MnO₂ had not been fully separated from the postreaction solution and a slight excess of hydrogen peroxide had been used in the course of the low temperature titration of permanganate and manganese. In carefully performed experiments the carbonates were produced in 6–7% yield. Small degrees of oxidation have been determined by a simplified method. The frozen content of the postreaction mixture has been treated with slight excess of 3–5% H₂O₂ to decompose unreacted MnO₄⁻ and MnO₄²⁻ to manganese dioxide, transferred to the vacuum reactor and acidified with 85% H₃PO₄. ¹⁴CO₂ originating from carbonates and ¹⁴CO₂ obtained at room temperature acidic oxidation of oxalic acid with undecomposed H₂O₂ and in the course of acidic oxidation of oxalic acid with manganese dioxide has been collected in the calibrated volume of the vacuum line, its total pressure, temperature and average specific radioactivity determined and the degree of oxidation of acetate calculated. In that way the eventual “overestimation” of the degree of reaction has been eliminated. The simple analytical method described has been used to follow the kinetics of the oxidation of acetate with permanganate in alkaline medium. In neutral medium this analytical procedure does not work. It was necessary to add a certain amount of sodium hydroxide to the postreaction mixture in order to decompose the manganate and permanganate with dilute H₂O₂. An alternate analytical procedure consisted of the case of acetate oxidation studies in treating the post reaction mixture cooled to room temperature with orthophosphoric acid. Oxalic acid, the product