

KINETICS AND MECHANISM OF OXIDATION OF TARTARIC ACID BY BROMATE IONS AND AN HETEROGENEOUS OSCILLATION REACTION OF TARTARIC ACID

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The kinetics and mechanism of oxidation of tartaric acid by bromate ions in sulphuric acid solutions have been studied. As the relation between the concentration of H_3O^+ ions and the reaction rate constant indicates, the species involved in the reaction are protonized bromate ions (HBrO_3) and tartaric acid molecules. Their interaction is of dipole-dipole nature, as borne out by measurements of the rate constant in dependence on the dielectric constant and on the ionic strength. The activation parameters and the stoichiometry of the reaction have been evaluated. An oscillation behaviour is observed in the presence of a Mn(II) catalyst if bromine is removed from the system constantly. The concentration ranges in which the oscillations occur have been established. Bromine is shown to play a major part in the heterogeneous oscillation system.

According to Noyes¹, oscillation reactions involving oxidations of organic substrates by bromate can be classed in five groups. The fourth group includes easily oxidized substrates such as oxalic acid^{2,3}, and redox catalysts. Oscillations of the metal catalyst or bromine only take place if the latter is removed from the reaction solution with an inert gas. We have found that tartaric acid can act as an organic substrate in a heterogeneous oscillation reaction of this kind⁴. Tartaric acid, as well as oxalic acid, is incapable of formation of bromo derivatives, in contrast to substrates for a classical Belousov-Zhabotinskii oscillation reaction. Tartaric acid (which is oxidized without bromination) has been used for a homogeneous oscillation reaction in a mixture with acetone⁵ (which is brominated, but not oxidized). Oscillation reactions with mixed substrates belong to the third group in Noyes' classification.

The aim of the present work was to gain insight into the kinetics of some partial reactions taking place in the oscillation system tartaric acid- BrO_3^- - Mn(II) - H_2SO_4 and to determine the concentration ranges in which oscillations take place in this system. Attention was paid particularly to the kinetics and mechanism of the oxidation-reduction reaction of bromate ions with tartaric acid, which had not been examined before. The rate constant of this reaction and the rate constants of reduction of Mn(III) and Ce(IV) ions by tartaric acid were measured.

EXPERIMENTAL

The kinetics of oxidation of tartaric acid by bromate ions was examined polarographically by recording the time dependence of the limiting diffusion current of BrO_3^- ions at potentials of -1.0 to -1.1 V against 1M mercurous sulphate electrode (M.S.E.). The oxidation of tartaric acid by bromine was monitored at a potential of -0.6 V vs M.S.E., corresponding to the limiting diffusion current of bromine in 1.5M- H_2SO_4 . A potential of -0.2 V vs M.S.E. was chosen for the reactions of Mn(III) and Ce(IV) ions with tartaric acid in 1.5M- H_2SO_4 . The time drop of the limiting diffusion current was followed until the reaction was at least 80% complete. The dependences were evaluated to give the rate constant values, largely by means of the integrated form of the 1st order kinetic equation.

The measurements were carried out on LP 7e (Laboratorní přístroje, Prague) and OH-105 (Radelkis, Budapest) polarographs. A Kalousek's polarographic vessel adapted for water thermostating, in conjunction with a U 3 ultrathermostat (Prüfgeräte-Werk, Medingen, GDR), served as the polarographic vessel. The rate constants reported are averages of three to five replicate measurements accomplished with a precision of $\pm 5\%$.

The heterogeneous oscillation reaction of BrO_3^- , H_2SO_4 , MnSO_4 , and $\text{C}_4\text{H}_6\text{O}_6$ was also monitored polarographically. The reaction was conducted in a thermostated reaction vessel, from which the volatile products were transferred into a Kalousek's vessel by means of a stream of nitrogen for bulbs. In the latter vessel the concentration of the only polarographically-active product, bromine, was determined continuously in 1.5M- H_2SO_4 at a potential of -0.6 V vs M.S.E. The nitrogen flow rate was held constant, usually at a value of 720 ml min^{-1} for 10 ml of reaction solution, by using a universal UPLS 3 flow meter.

The chemicals used were of reagent grade purity, the solution were made up from redistilled water.

Solution of Mn(III) was prepared by reduction of permanganate with a slight excess of manganese(II) sulphate in 5M- H_2SO_4 .

RESULTS AND DISCUSSION

Oxidation of Tartaric Acid by Bromate Ions

In the presence of a high excess of tartaric acid, the time dependence of the limiting diffusion current of BrO_3^- ions, in the form $\ln(i_0/i) = f(t)$, is not linear; instead, it exhibits an autocatalytic nature. Tartaric acid reacts with bromate ions to give bromine, which is reduced by tartaric acid to bromide. Bromate ions are removed from the reaction mixture on account of the reaction not only with tartaric acid, but also with bromide ions. A rate equation for the autocatalytic process has been derived previously⁷ for the reaction of oxalic acid with bromate ions. If the bromine formed is removed from the solution by purging with nitrogen, the $\ln(i_0/i) = f(t)$ plot acquires a linear shape, thus losing its autocatalytic character and indicating that the process is 1st order with respect to bromate ions. An identical result is obtained if mercuric acetate is added to the solution to mask the bromide ions: the $\ln(i_0/i) = f(t)$ dependence is linear and the corresponding rate constant agrees with that obtained in the heterogeneous conditions, i.e. with nitrogen purging. At a constant nitrogen flow rate of 720 ml min^{-1} for 10 ml of bromine solution in

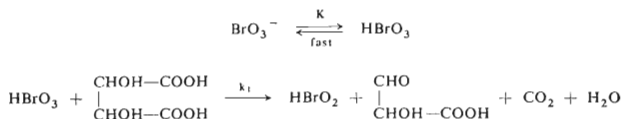
1.5M-H₂SO₄, the concentration of bromine decreases with a half-life of 28 s. When recording the polarographic current in preselected time intervals, the nitrogen feed was discontinued always for about 10 s.

Logarithmic analysis evidenced that the reaction is 1st order also with respect to tartaric acid. The concentration of the latter was varied over the region of 0.08 to 1.0 mol l⁻¹ (the concentration of bromate was 0.5 mmol l⁻¹, the solvent was 1.5M-H₂SO₄). The rate equation, for a constant concentration of hydrogen ions, thus is

$$-d[\text{BrO}_3^-]/dt = k[\text{BrO}_3^-][[\text{C}_4\text{H}_6\text{O}_6]]. \quad (1)$$

The 2nd order rate constant, for 1.5M-H₂SO₄ and a temperature of 25°C, is $k = 9.1 \cdot 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$.

The reaction under study is acid catalyzed; at a constant ionic strength the rate constant increases with increasing concentration of H₃O⁺ ions. Tartaric acid in sulphuric acid solutions is slightly dissociated to the first degree ($K_1 = 1.04 \cdot 10^{-3}$) and practically nondissociated to the second and third degrees ($K_2 = 4.55 \cdot 10^{-5}$, $K_3 = 2 \cdot 10^{-15}$; ref.⁶). The species entering the reaction with bromate thus is essentially nondissociated tartaric acid. The dependence of the logarithm of the rate constant on the logarithm of the hydrogen ion concentration gives a linear plot with a slope of unity, indicating that a single proton is exchanged. In so acid solutions (0.6 to 2M-H₂SO₄) bromate ions give bromic acid, a strong oxidant, and the reaction probably involves protonated bromate ions (HBrO₃) and tartaric acid molecules. The assumed mechanism,

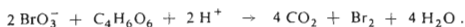


implies the validity of Eq. (2),

$$-d[\text{BrO}_3^-]/dt = k_1 K [\text{H}^+] [\text{BrO}_3^-] [\text{C}_4\text{H}_6\text{O}_6], \quad (2)$$

accounting well for the observed effects.

The overall stoichiometry of the reaction of bromate with tartaric acid is described by the equation



The takeup of two bromate ions per molecule of tartaric acid was found by amperometric titrations.

The rate of oxidation of tartaric acid by bromate was examined also in dependence on the dielectric constant; acetic acid was added to the reaction system and the dielectric constant values for water-acetic acid mixtures were taken from ref.⁸. According to Kirkwood's theory for dipole-dipole interactions, a linear plot, with a negative slope, should be obtained in the coordinates of $\ln k$ and $(\epsilon - 1)/(2\epsilon + 2)$. Our measurements, actually giving a negative slope (Fig. 1), bear out the assumption that the reacting species are molecules, *viz.* those of bromic acid and of tartaric acid. This is also corroborated by the fact that at a constant concentration of H_2SO_4 and a constant temperature, a variation in the ionic strength, from 0.8 to 2.0 mol l^{-1} , did not affect the rate constant; the values corresponding to the two limiting ionic strengths were $3.6 \cdot 10^{-4}$ and $3.5 \cdot 10^{-4}$ l mol $^{-1}$ s $^{-1}$, respectively.

The activation parameters of the reaction, as derived from the temperature dependence of the rate constant by means of Eyring's equation, are $\Delta H^\ddagger = 60.8$ kJ . mol $^{-1}$ and $\Delta S^\ddagger = -99$ J K $^{-1}$ mol $^{-1}$. The negative value of the activation entropy implies a higher degree of ordering, a higher compactness, of the activated complex as compared with the initial state. It is conceivable that a cyclic ester is formed as the activated complex, decomposing then to the products; the occurrence of such a cyclic ester has been suggested⁹ for the oxidation of α -hydroxy acids by bromate ions. No cyclic ester can appear in the oxidation of oxalic acid by bromate ions, and the activation entropy actually is higher^{7,10}.

Oxidation of Tartaric Acid by Bromine

The rate of oxidation of tartaric acid by bromine was evaluated by the method of Herbine, Brummer and Field¹¹, whose studied the oxidation of formic acid by bro-

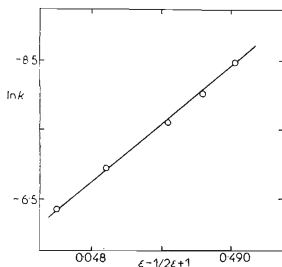


FIG. 1

Dependence of $\ln k$ on the dielectric constant. $c_{\text{BrO}_3^-} = 0.5$ mmol l^{-1} , $c_{\text{C}_4\text{H}_6\text{O}_6} = 0.2$ mol . l^{-1} ; 1.5-M H_2SO_4 , 25°C

mine in strongly acid solutions. The authors assume that Br_3^- ions are formed through a rapidly establishing equilibrium



The concentration of bromine, at a constant concentration of hydrogen ions, then decreases as

$$-d[\text{Br}_2]'/dt = k[\text{Br}_2][\text{C}_4\text{H}_6\text{O}_6], \quad (3)$$

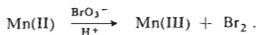
where $[\text{Br}_2]'$ is the total analytical concentration of bromine, present as Br_2 or Br_3^- . The rate constant, in 1.5M- H_2SO_4 at 20°C, is $k = 1.8 \cdot 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$.

Oxidation of Tartaric Acid by Mn(III) and Ce(IV) Ions

Only the apparent rate constants of oxidation of tartaric acid by Mn(III) and Ce(IV) ions were determined in the conditions used for the oscillation reaction, *viz.* $c_{\text{C}_4\text{H}_6\text{O}_6} = 30 \text{ mmol l}^{-1}$, $c_{\text{Mn}} = c_{\text{Ce}} = 0.1 \text{ mmol l}^{-1}$, solutions in 1.5M- H_2SO_4 , temperature 20°C. The rate constants for Mn(III) and Ce(IV) were $5.1 \cdot 10^{-3}$ and $8.7 \cdot 10^{-4} \text{ s}^{-1}$, respectively.

The Oscillation System

If a Mn(II) catalyst is added to the reaction mixture of tartaric acid with bromate ions in 1.5M- H_2SO_4 , the system will exhibit oscillation behaviour provided that bromine is removed constantly. This oscillation reaction belongs to the group of heterogeneous oscillation reaction in which the organic substrate is a molecule incapable of formation of bromo derivatives. Oscillations of the Mn(II)—Mn(III) concentration were observed visually in the reaction vessel. The characteristic pink colour due to Mn(III) was accompanied by an increase in the concentration of bromine in the Kalousek's vessel in which its variations were monitored (Fig. 2). It follows from the mechanism of the Belousov-Zhabotinskii oscillation reaction that the oscillations of the concentrations of the oxidized and the reduced forms are due to periodic variations in the concentration of bromide ions about its critical value, while in the oscillation reaction of the heterogeneous type they appear as a result of the periodic change in the concentration of bromine³. Up to the critical concentration of bromine the autocatalytic oxidation of Mn(II) by bromate can take place:



After the bromine concentration surpasses the critical value, this reaction does not

occur and regeneration takes place:

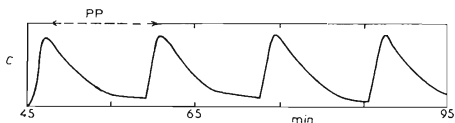
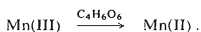


FIG. 2

Oscillations of the bromine concentration (in arbitrary units) in the heterogeneous oscillation reaction with tartaric acid within 45 min. $c_{\text{BrO}_3^-} = 8 \text{ mmol l}^{-1}$, $c_{\text{C}_4\text{H}_6\text{O}_6} = 30 \text{ mmol l}^{-1}$, $c_{\text{Mn(II)}} = 3 \text{ mmol l}^{-1}$; 1.5M- H_2SO_4 , 20°C, nitrogen flow rate 1 100 ml min^{-1} , solution volume 10 ml

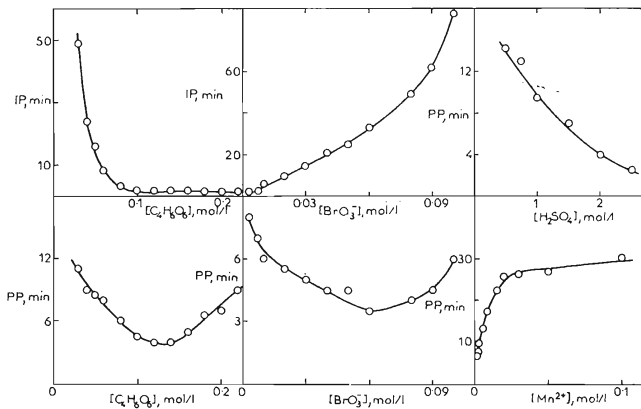


FIG. 3

Dependence of the induction period (IP) and oscillation period (PP) on the concentrations of the components. $c_{\text{BrO}_3^-} = 7 \text{ mmol l}^{-1}$, $c_{\text{C}_4\text{H}_6\text{O}_6} = 80 \text{ mmol l}^{-1}$, $c_{\text{Mn(II)}} = 3 \text{ mmol l}^{-1}$; 1.5M- H_2SO_4 , 20°C, nitrogen flow rate 720 ml min^{-1} , solution volume 10 ml

By this reaction the reduced form of the catalyst, necessary for the preceding reaction, is recovered. The reaction of bromine with tartaric acid is too slow ($k = 1.8 \cdot 10^{-3} \text{ l} \cdot \text{mol}^{-1} \text{ s}^{-1}$) to enable the formation of bromide ions, and so we assume that it is bromine that plays a major role in the oscillation behaviour of the system under study. The range of existence of oscillations can be identified with the range in which the bromine concentration can oscillate about its critical value. Such oscillations can only occur at certain rates of accumulation and of takeup of bromine. By varying the flow rate of nitrogen, the time necessary for the attainment of the critical bromine concentration, and thereby the oscillation period, is changed.

At a constant flow rate of nitrogen of 720 ml min^{-1} and in the presence of Mn(II) in a concentration of 3 mmol l^{-1} , our system oscillates, since for the initial concentration $[\text{BrO}_3^-]_0 = 7 \text{ mmol l}^{-1}$ we have $0.035 < [\text{BrO}_3^-]_0/[\text{C}_4\text{H}_6\text{O}_6]_0 < 0.23$, and for $[\text{C}_4\text{H}_6\text{O}_6]_0 = 80 \text{ mmol l}^{-1}$, $0.037 < [\text{BrO}_3^-]_0/[\text{C}_4\text{H}_6\text{O}_6]_0 < 1.25$.

Based on the time variations of the bromine concentration, the dependences of the induction period (IP) and of the oscillation period (PP) on the concentrations of the system components could be established (Fig. 3). By induction period is meant the time after which the system starts to oscillate. This should not be confused with the time after which reaction (3) sets in; this reaction has its own induction period if considered in analogy with the reaction of Ce(III) with bromate¹². In fact, bromine appears immediately after the mixing of the reactants, but its concentration remains constant as though it were removed physically at the same rate at which it is formed. Only after its concentration drops below the critical value the oscillations of the system commence. If the concentration of tartaric acid is eight times as high as that of bromate ions, the system oscillates from the very beginning, without any induction period. Thus, during the induction period the reactions occurring adjust the concentrations of the starting substances so that the conditions become favourable for oscillations. The induction period was very little dependent on the concentrations of sulphuric acid and manganese(II) ions.

Ce(III) ions fail to act as a catalyst in the oscillation reaction with tartaric acid, probably because the step in which their reduced form is created is too slow. As our data show, the oxidation of tartaric acid by Ce(IV) ions is six times slower than by Mn(III) ions.

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