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A kinetic study of D-glucose oxidation by bromine in aqueous solutions

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Abstract—The kinetics of the oxidation of D-glucose to D-gluconic acid by bromine in aqueous solution were studied using potentiometric techniques and theoretical considerations of complex bromine–bromide–pH equilibria. The pH has a strong influence on reaction rate. At pH < 8 the reaction is very slow, while in the pH range pH 8–9.5 the reaction is sufficiently fast and seems optimal for the reaction. The proposed active species at that pH region is hypobromous acid. At pH > 9.5, the reaction is further accelerated due to the formation of hypobromite.
The proposed kinetics expression for gluconic acid formation, based on the determined kinetic parameters at pH 9.24, is of the form

$$dc(GA)/dt = 160c^2(G)c_0(HOBr)c^0(H^+)c^0(Br)$$

Keywords: Bromine; D-Glucose; D-Gluconic acid; Hypobromous acid; Oxidation; Indirect electroorganic synthesis

1. Introduction

Indirect electroorganic synthesis is based on the electrochemical production of a halide active species in situ, which reacts in solution with organic reactants. In general, the reaction is very important due to a high-efficiency process that is easy to carry out. Examples of these reactions include the production of gluconic acid or calcium gluconate by glucose oxidation[1–3] or xylonic acid from xylose[4] with electrochemically generated bromine, or indirect oxidation of cyclohexanol to cyclohexanone with iodine.[5]

D-Glucose oxidation in aqueous solutions containing bromine is shown in Eq. 1

$$\text{D-glucose} + Br_2 + H_2O \rightarrow \text{D-gluconic acid} + 2HBr \quad (1)$$

This reaction is a well-known reaction found in organic chemistry textbooks,[6] but there is a lack of information concerning the kinetics of this oxidation. The earliest studies of electrochemical glucose oxidation to gluconic acid were carried out by Isbell and co-workers.[7,8] Bromine ions in the presence of calcium carbonate were first electrochemically oxidized to hypobromite, which chemically oxidized glucose via a δ-gluconolactone intermediate. Fink and Summers[9] found that the optimum electrolyte composition for electrolysis in the semi-industrial production of calcium gluconate was 0.8 M D-glucose and 0.17 M sodium bromide. Even though such a process gives a high yield of product without by-products, it has been replaced with enzymatic processes[10] with long reaction times and relatively low selectivity or by oxidation with air in the presence of noble metal catalysts, which can be easily deactivated over time.[11–13] The main reasons for giving up the electrochemical process were use of degradable carbon anodes

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and the high cost of electric power at that time. Today, dimension-stable anodes (DSA) are widespread and the cost of electric power is comparably less. One more advantage of electrochemical processes is the possibility of paired electroorganic synthesis, for example, the production of D-gluconic acid and D-glucitol (sorbitol) at the same time.[2,3] Hence, consideration of electrochemical production of D-gluconic acid or D-gluconates is again of interest, and a detailed kinetics study should be the first step in processes optimization.

In aqueous solutions on an indicator electrode (e.g., Pt), bromine in the presence of free electrons establishes a bromine–bromide electrochemical equilibrium:[14]

$$(\mathrm{Pt})\mathrm{Br_2} + 2\mathrm{e} \leftrightarrows 2\mathrm{Br}^- \tag{2}$$

or in the presence of bromide ions, a tribromide is formed:

$$(\mathrm{Pt})\mathrm{Br_3}^- + 2\mathrm{e} \leftrightarrows 3\mathrm{Br}^- \tag{2a}$$

The equations describing the changes of equilibrium potentials, E_r, are defined as

$$E_r(\mathrm{Br_2}|\mathrm{Br}^-) = E_r^{\theta}(\mathrm{Br_2}|\mathrm{Br}^-) - \frac{2.303RT}{2F}\log\frac{a^2(\mathrm{Br}^-)}{a(\mathrm{Br_2})}$$
$$E_r^{\theta} = 1.0874\ \mathrm{V} \tag{3}$$

and

$$E_r(\mathrm{Br_3}^-|\mathrm{Br}^-) = E_r^{\theta}(\mathrm{Br_3}^-|\mathrm{Br}^-) - \frac{2.303RT}{2F}\log\frac{a^3(\mathrm{Br}^-)}{a(\mathrm{Br_3}^-)}$$
$$E_r^{\theta} = 1.053\ \mathrm{V} \tag{3a}$$

where E_r^{θ} refers to standard equilibrium potentials. After rearrangements, these equations can be used to monitor bromine or tribromide activities over time, where $E_r(t)$ is the potential as a function of time:

$$a(\mathrm{Br_2}) = \frac{a^2(\mathrm{Br}^-)}{10^{\left[-\frac{2F[E_r(t)-E_r^{\theta}]}{2.303RT}\right]}} \tag{4}$$

or

$$a(\mathrm{Br_3}^-) = \frac{a^3(\mathrm{Br}^-)}{10^{\left[-\frac{2F[E_r(t)-E_r^{\theta}]}{2.303RT}\right]}} \tag{4a}$$

(*Note*: in dilute aqueous solutions, activities can be approximately replaced by concentrations.)

As a consequence, the kinetics of D-glucose oxidation can be monitored in situ by measuring electrochemical potential in time (potentiometry).

In this paper, we present the kinetic studies of D-glucose oxidation by bromine in aqueous solution, with consideration of the various thermodynamic equilibria, present in solution as a function of pH.

2. Experimental

Potentiometric titration was used to study the kinetics of D-glucose oxidation to D-gluconic acid. Pt mesh served as the indicator electrode, and a saturated calomel electrode ($E_r = 0.243$ V) served as the reference electrode. All equilibrium potentials in this study are given versus the standard hydrogen electrode. The potential measurements were carried out with a PAR 273 potentiostat controlled by a computer through a GPBI PC2A interface.

In order to determine the parameters of D-glucose oxidation, solutions of bromine and D-glucose were obtained by dissolution of stock solutions, using buffers to maintain constant pH.

The bromine stock solution, concentration of 0.1 M in 0.2 M KBr, was obtained by dissolving KBr and calculated volume of the liquid bromine ($\rho = 3.1\ \mathrm{g\ cm^{-3}}$) in doubly distilled water. This solution was protected from photolytic degradation by storing in a dark, cold place. The stock solution of D-glucose (2.50 M) was prepared by dissolving solid, anhydrous α-D-glucose (p.a. E. Merck) in doubly distilled water. This solution after storage, due to mutarotation, can be treated as an anomeric mixture of α and β isomers.

The buffer solutions used were as follows: for the pH interval of 7.50–9.24 a combination of 0.05 M sodium tetraborate (borax) and 0.1 M HCl (Titrival); for the pH interval of 9.24–12.4 a combination of 0.05 M sodium tetraborate and 0.10 M NaOH, and for pH 4.01 and 12.9, 0.05 M potassium diphthalate and 0.10 M NaOH, respectively.

The relative volumes of the solutions of borax and HCl or NaOH required for a total volume of 100 mL at a given pH are shown in Figure 1.

Equilibrium potential measurements were performed by adding bromine stock solutions (3–10 ± 0.01 mL) to the 100 mL of buffer solutions stirred by a magnetic stirrer. After a stabile value of the equilibrium potential had been established, D-glucose stock solution was

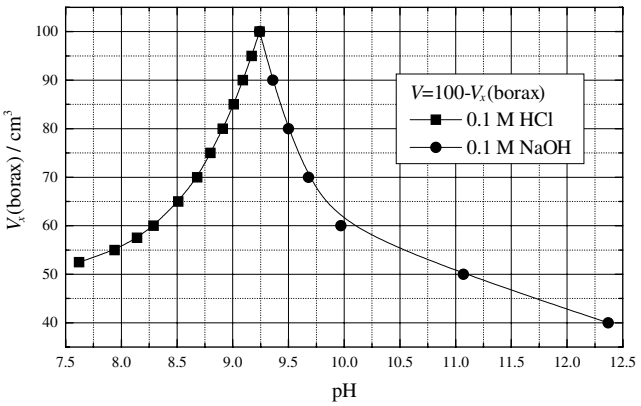

Figure 1. Required volume of 0.05 M sodium tetraborate for buffer solution preparation of 100 mL combined with 0.10 M HCl or 0.10 M NaOH.

added (0.2–3 ± 0.01 mL), taking this time as $t = 0$. It was assumed that addition of usually 3.2 mL to maximum 10 mL of stock solutions in 100 mL of a buffer solution does not change pH significantly. All experiments were performed at a temperature of 25 °C. A circulating constant-temperature bath maintained the temperature of the electrolyte within ±0.5 °C. Temperature control was done by thermometer with an accuracy of ±0.1 °C.

3. Results and discussion

Figure 2a shows the time dependence of the equilibrium potential at the Pt indicator electrode [(Pt)Br_2(aq)|Br^-(aq)] in solution containing 3 mM of total bromine and 0.20 M KBr after addition of 75 mM of D-glucose. It can be seen that the potential changes are very slow, over ~3000 s only ~20 mV. By using Eqs. 4 and 4a, the changes of bromine and tribromide concentrations over time can be calculated. These are shown in the inset of Figure 2.

The following conclusions can be made based on the data from Figure 2.

(a) The calculated initial concentration of free bromine in the solution at $t = 0$ was ~1 mM, which is approximately three times smaller compared to the concentration of totally added bromine (3 mM). This is probably due to a rapid reaction between bromine and bromide ions (Eq. 2a), with formation of tribromide ions. The calculated initial concentration for tribromide ions was ~3 mM.

(b) The oxidation of D-glucose by bromine is a pseudo first-order reaction with respect to bromine. This can be determined from the linear dependences of the logarithm of the bromine and tribromide concentrations as a function of time.

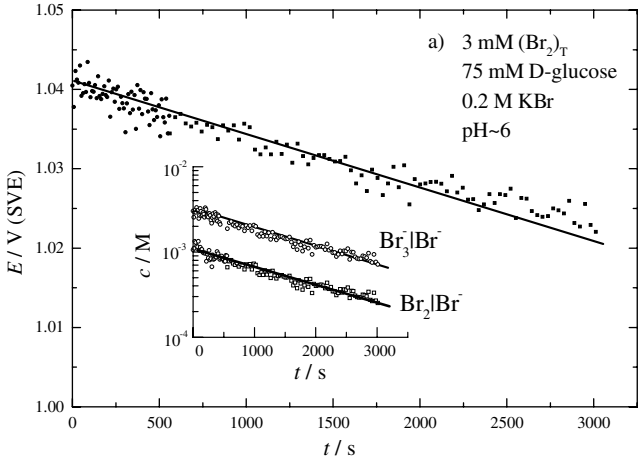

Figure 2. Time dependence of equilibrium potential after addition of D-glucose. Inset: Time dependences of bromine and tribromide concentrations as calculated from Eqs. 4 and 4a.

(c) The establishment of chemical equilibria and formation of tribromide as well as hypobromous acid and hypobromite at different pH of the solutions should be considered.

In aqueous solutions, the dependence of bromine and bromide ion concentration at the pH of the solution is very complex. In order to determine which of the bromine species is dominant at a specific pH, the following thermodynamic analysis was carried out, based on the known chemical reactions in this complex system.

In aqueous solutions of bromide ions and bromine the following chemical equilibria are observed.[15,16]

(1) Disproportionation with formation of hypobromous acid and bromide ions:

$$Br_2 + 2H_2O \overset{K_1^\theta}{\rightleftarrows} HOBr + H_3O^+ + Br^- \quad (5)$$

The standard chemical equilibrium constant for the reaction, K_1^θ, is equal to its formal equilibrium constant, K_1, keeping in mind that $\Sigma v = 0$:

$$K_1^\theta = K_1 = \frac{a(HOBr)a(H_3O^+)a(Br^-)}{a(Br_2)a^2(H_2O)} = 7.2 \times 10^{-9} \quad (5a)$$

(2) Dissociation of hypobromous acid to hypobromite and a proton:

$$HOBr + H_2O \overset{K_2^\theta}{\rightleftarrows} BrO^- + H_3O^+ \quad (6)$$

$$K_2^\theta = K_2 = \frac{a(BrO^-)a(H_3O^+)}{a(HOBr)a(H_2O)} = 2 \times 10^{-9} \quad (6a)$$

(3) Disproportionation with formation of hypobromite and bromide ions:

$$Br_2 + 2OH^- \overset{K_3^\theta}{\rightleftarrows} BrO^- + Br^- + H_2O \quad (7)$$

$$K_3^\theta = K_3 = \frac{a(BrO^-)a(Br^-)a(H_2O)}{a(Br_2)a^2(OH^-)} = 2 \times 10^{8} \quad (7a)$$

Formation of tribromide ions:

$$Br_2 + Br^- \overset{K_4^\theta}{\rightleftarrows} Br_3^- \quad (8)$$

$$K_4^\theta = \frac{a(Br_3^-)}{a(Br_2)a(Br^-)} = 16.85\ M^{-1} \quad (8a)$$

The mass-balance equation with respect to free bromine, $c(Br)_s$, in the solution can be used to determine the concentration of the bromine species as a function of pH (*Note*: for a detailed analysis, see Supplementary data), with the approximation that activities could be

replaced by concentrations and that water has unity activity:

$$c(\mathrm{Br_2})_s = c(\mathrm{Br_2})_T - c(\mathrm{Br_3^-}) - c(\mathrm{HOBr}) - c(\mathrm{BrO^-}) - c(\mathrm{BrO^-})_{\mathrm{HOBr}} \quad (9)$$

where $c(\mathrm{Br_2})_T$ is the total analytical concentration of bromine in the solution and $c(\mathrm{BrO^-})_{\mathrm{HOBr}}$ is the concentration of hypobromite ions, produced by hydrolysis of hypobromous acid, given by

$$c(\mathrm{BrO^-})_{\mathrm{HOBr}} = \frac{K_2 c(\mathrm{HOBr})}{c(\mathrm{H_3O^+})} \quad (10)$$

Dividing Eq. 9 by $c(\mathrm{Br})_s$, the following was obtained:

$$1 = \frac{c(\mathrm{Br_2})_T}{c(\mathrm{Br_2})_s} - \frac{c(\mathrm{Br_3^-})}{c(\mathrm{Br_2})_s} - \frac{c(\mathrm{HOBr})}{c(\mathrm{Br_2})_s} - \frac{c(\mathrm{BrO^-})}{c(\mathrm{Br_2})_s} - \frac{c(\mathrm{BrO^-})_{\mathrm{HOBr}}}{c(\mathrm{Br_2})_s} \quad (11)$$

Finally, after introducing Eqs. 5a–8a and 10 in Eq. 11 and rearranging, the concentration of free bromine in the solution as a function of pH was obtained:

$$c(\mathrm{Br_2})_s = c(\mathrm{Br_2})_T \left[1 + K_4^\theta c(\mathrm{Br^-}) + \frac{K_1}{c(\mathrm{Br^-})c(\mathrm{H_3O^+})} + \frac{K_3 c^2(\mathrm{OH^-})}{c(\mathrm{Br^-})} + \frac{K_1 K_2}{c(\mathrm{Br^-})c^2(\mathrm{H_3O^+})}\right]^{-1} \quad (12)$$

By an analogous procedure, once the dependence of the free bromine concentration on pH is known, it is also possible to calculate the pH dependence of the concentration of all other species in the solution.

For hypobromous acid

$$c(\mathrm{HOBr}) = -c(\mathrm{Br_2})_s \left(1 + \frac{K_2}{c(\mathrm{H_3O^+})}\right)^{-1} \left(1 - \frac{c(\mathrm{Br_2})_T}{c(\mathrm{Br_2})_s} + K_4^\theta c(\mathrm{Br^-}) + \frac{K_3 c^2(\mathrm{OH^-})}{c(\mathrm{Br^-})}\right) \quad (13)$$

for total hypobromite ions

$$c(\mathrm{BrO^-}) = -c(\mathrm{Br_2})_s \left(1 - \frac{c(\mathrm{Br_2})_T}{c(\mathrm{Br_2})_s} + K_4^\theta c(\mathrm{Br^-}) + \frac{K_1}{c(\mathrm{Br^-})c(\mathrm{H_3O^+})}\right) \quad (14)$$

and for tribromide ions

$$c(\mathrm{Br_3^-}) = -c(\mathrm{Br_2})_s \left(1 - \frac{c(\mathrm{Br_2})_T}{c(\mathrm{Br_2})_s} + \frac{K_1}{c(\mathrm{H_3O^+})c(\mathrm{Br^-})} + \frac{K_3 c^2(\mathrm{OH^-})}{c(\mathrm{Br^-})} + \frac{K_1 K_2}{c(\mathrm{Br^-})c^2(\mathrm{H_3O^+})}\right) \quad (15)$$

Based on the analysis given above, the theoretical pH dependence of concentration of all considered bromine species in the solution is given in Figure 3. for a total bromine concentration, $c(\mathrm{Br_2})_T$, of 3 mM in a solution of 0.20 M KBr.

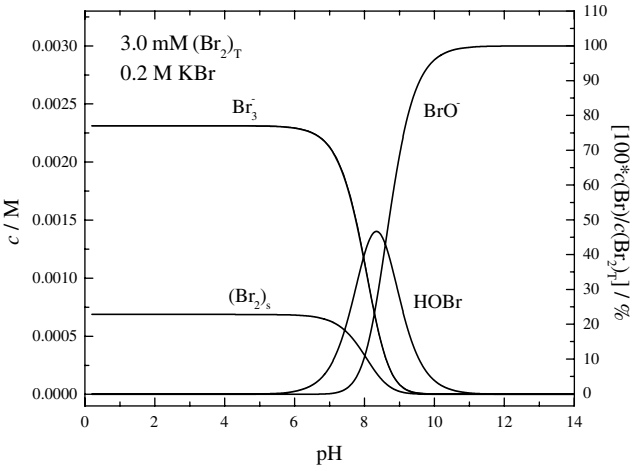

Figure 3. Concentration (left) and percentage (right) pH distribution of bromine species in a solution of 3 mM of total bromine in 0.20 M KBr.

As it can be seen in Figure 3, the pH of the solution has great influence on the bromine species distribution, which, on the other hand, could have great influence on the kinetics of the D-glucose oxidation. At pH lower than pH 6, the dominant species are free bromine and tribromide ions, present at ~23% and 77%, respectively. At pH greater than pH 6, the concentrations of free bromine and tribromide ions decrease, while the concentrations of hypobromous acid and hypobromite ions increase. The maximum concentration of hypobromous acid is realized at pH 8.3 (ratio of ~47 %), after which it decreases due to dissociation into hypobromite and a proton.

The presence of different bromine species in the solution also leads to establishment of different electrochemical equilibria that are characterized by their own equilibrium potentials:

$$\mathrm{Br_2} + 2\mathrm{e} \leftrightarrows 2\mathrm{Br^-} \quad (16)$$

$$E_r = E_r^\theta(\mathrm{Br_2}|\mathrm{Br^-}) - \frac{2.303RT}{2F}\log\frac{c^2(\mathrm{Br^-})}{c(\mathrm{Br_2})} \quad E_r^\theta = 1.0874\ \mathrm{V} \quad (17)$$

$$\mathrm{Br_3^-} + 2\mathrm{e} \leftrightarrows 3\mathrm{Br^-} \quad (18)$$

$$E_r = E_r^\theta(\mathrm{Br_3^-}|\mathrm{Br^-}) - \frac{2.303RT}{2F}\log\frac{c^3(\mathrm{Br^-})}{c(\mathrm{Br_3^-})} \quad E_r^\theta = 1.0503\ \mathrm{V} \quad (19)$$

$$\mathrm{HOBr} + \mathrm{H_3O^+} + 2\mathrm{e} \leftrightarrows \mathrm{Br^-} + 2\mathrm{H_2O} \quad (20)$$

$$E_r = E_r^\theta(\mathrm{HOBr}|\mathrm{Br^-}) - \frac{2.303RT}{2F}\log\frac{c(\mathrm{Br^-})}{c(\mathrm{HOBr})c(\mathrm{H_3O^+})} \quad E_r^\theta = 1.33\ \mathrm{V} \quad (21)$$

$$\mathrm{BrO^-} + \mathrm{H_2O} + 2\mathrm{e} \leftrightarrows \mathrm{Br^-} + 2\mathrm{OH^-} \quad (22)$$

$$E_r = E_r^{\theta}(\mathrm{BrO^-}|\mathrm{Br^-}) - \frac{2.303RT}{2F}\log\frac{c(\mathrm{Br^-})c^2(\mathrm{OH^-})}{c(\mathrm{BrO^-})}$$

$$E_r^{\theta} = 0.761\ \mathrm{V} \qquad (23)$$

Formation of the D-gluconic acid from D-glucose can be described by the general kinetic equation:

$$\frac{\mathrm{d}c(\mathrm{GA})}{\mathrm{d}t} = kc^p(\mathrm{G})c^q(\mathrm{Br})c^r(\mathrm{H^+})c^s(\mathrm{Br^-}) \qquad (24)$$

where GA and G refer to D-gluconic acid or D-gluconate and D-glucose, respectively. Br is the bromine species participating in the reaction, k is the rate constant, and p, q, r, and s refer to partial reaction orders of the participants in the reaction.

As already mentioned, the pH has great influence on the bromine species distribution. Therefore, its influence on the rate formation of D-gluconic acid was investigated first. The results are given in Figure 4. The experimental conditions had been chosen in such a way that the starting concentrations of D-glucose and bromide ion were scientifically greater than the total bromine concentration, in order to insure pseudo first-order conditions with respect to bromine, at the beginning of the reaction.

As can be seen in Figure 5, the reaction practically does not take place at pH 4.0 and 6.0, that is, only extremely small changes of potential were observed in a short period. Hence, it could be concluded that free bromine and tribromide ions are only weakly active in the oxidation of D-glucose. With increasing pH, the reaction accelerates and in the range of pH 6–10 after introducing D-glucose into the solution, significant changes in the equilibrium potential were observed. With further increase of the pH, at pH $\geqslant$ 10, the reaction further accelerates, followed by a rapid drop of potential in less than 5 s (Fig. 4). With the assumption of pseudo first-order with respect to bromine, the slope ($\mathrm{d}E_r/\mathrm{d}t$) should be

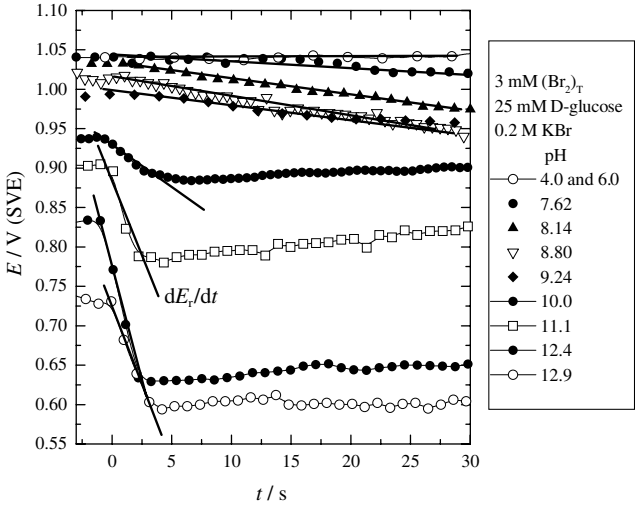

Figure 4. Time dependence of equilibrium potentials at different pH values of the solution.

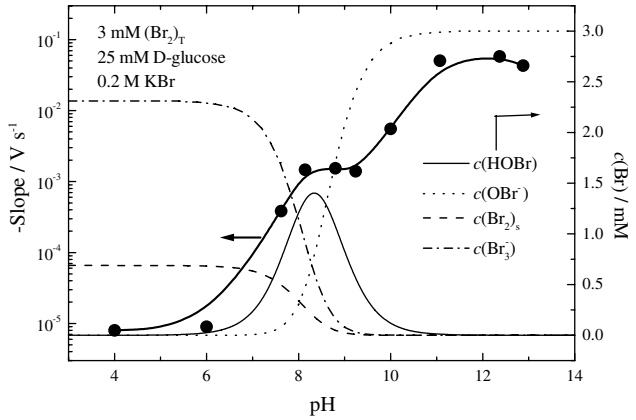

Figure 5. pH dependence of the slopes obtained from linear parts of the curves in Figure 4 compared with theoretical distribution curves of bromine species.

proportional to the pseudo first-order rate constants. The actual values of the slope as a function of pH are given in Figure 5 (bold line) and are compared to the theoretical distribution of the bromine species, as established earlier (Fig. 3).

Since the value of the slope is proportional to the rate constant, the dependence of the logarithm of the slope on the logarithm of the hydrogen-ion concentration, that is, pH, $\mathrm{pH} = -\log a(\mathrm{H^+})$, directly gives the reaction order with respect to pH. It follows that in the pH region between pH ~6 and 8, the reaction order with respect to $\mathrm{H^+}$ is about −1; in the region between pH ~8 and 9.5, the order is ~0; in the region between pH ~9.5 and 11, about −1, and at even greater pH again around ~0. If these results are compared with the distribution curves of the bromine species as a function of pH (Fig. 3), the rate of the reaction can be matched with a particular bromine species. In the pH region between pH ~7 and ~9.5, the dominant species should be hypobromous acid, while at higher pH, the dominate species could be hypobromite ion. All this illustrated the complexity of the D-glucose oxidation with $\mathrm{Br_2}$, which results from the existence of various equilibria in the bromine–bromide ion system.

Considering that in acid and in weakly acidic solutions, the D-glucose oxidation does not effectively take place, the optimum conditions for the reaction would be alkaline, that is, pH > 10. However, in alkaline solution, even at room temperature, the disproportionation reaction of hypobromite ions to bromate and bromide ions occurs according to:[14]

$$3\mathrm{BrO^-} \leftrightarrows \mathrm{BrO_3^-} + 2\mathrm{Br^-} \qquad (25)$$

Although as shown in Figure 6, the bromate ion is a relatively strong oxidant that can, in principle, oxidize D-glucose, it is obvious from Eq. 25 that 2 mol of the active $\mathrm{BrO^-}$ species is lost, which diminishes the overall effectiveness of the reaction.

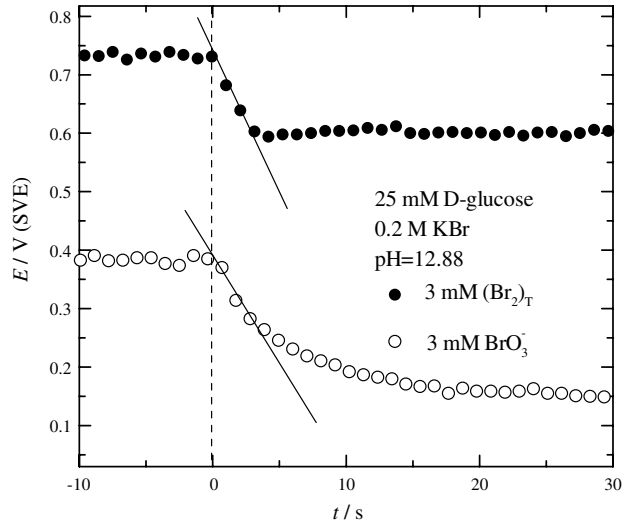

Figure 6. Comparison of time dependence of equilibrium potentials after introduction of D-glucose into a solution containing 3 mM bromine and 3 mM bromate ions.

Hence, the optimal pH for D-glucose oxidation lies between pH 8 and 9.5. Another advantage of operating in weakly alkaline solution is the faster hydrolysis of the initial reaction product (D-glucono-1.5-lactone) of D-glucose to D-gluconic acid or at this pH to D-gluconate. Fast hydrolysis of D-glucono-1.5-lactone in weak alkaline media is completed in few minutes, while in acid media this reaction is very slow.[17]

Figure 7 shows time dependences of equilibrium potentials for different concentrations of total added bromine at pH 9.24, while holding the concentrations of D-glucose and bromide ion constant.

It can be seen that for the first 60 s, the time dependence of the potential is essentially linear. Since it was assumed that the active species in the reaction is hypobromous acid due to the highest standard potential equation 21, and that its concentration differs from the concentration of total added bromine, the problem of determining the hypobromous acid concentration arises. For that reason, the actual concentration of hypobromous acid was calculated using a rearranged form of Eq. 21 (solved for c(HOBr) starting with the concentration c_0(HOBr) at time $t = 0$). Again assuming a pseudo first-order dependence, the following can be written:

$$\frac{\mathrm{d}c(\mathrm{GA})}{\mathrm{d}t} = -\frac{\mathrm{d}c(\mathrm{HOBr})}{\mathrm{d}t} = k'c(\mathrm{HOBr}) \qquad (26)$$

where k' is the pseudo first-order rate constant, $k' = kc^p(\mathrm{G})c^s(\mathrm{Br}^-)$.

Integrating Eq. 26 and introducing for $t = 0$, $c(\mathrm{HOBr}) = c_0(\mathrm{HOBr})$, one obtains

$$\log\frac{c(\mathrm{HOBr})}{c_0(\mathrm{HOBr})} = -\frac{k'}{2.303}t \qquad (27)$$

Figure 8 shows the time dependence of the ratio of the logarithms of actual and zero time concentrations of hypobromous acid, calculated using the rearranged Eq. 21. Through this procedure, a family of straight lines with essentially identical slopes was obtained. This is a confirmation of the pseudo first-order assumption.

Based on Eq. 27, the slope seen in Figure 8 is proportional to the pseudo first-order rate constant, and the average value of the rate constant is $k' = -2.303 \times \mathrm{slope} = 0.075 \pm 0.01\ \mathrm{s}^{-1}$.

On the other hand, considering Eq. 21 and a rearranged Eq. 27:

$$E_\mathrm{r} = E_\mathrm{r}^{\theta}(\mathrm{HOBr}|\mathrm{Br}^-) - \frac{2.303RT}{2F}\log\frac{c(\mathrm{Br}^-)}{c(\mathrm{HOBr})c(\mathrm{H_3O^+})} \qquad (21)$$

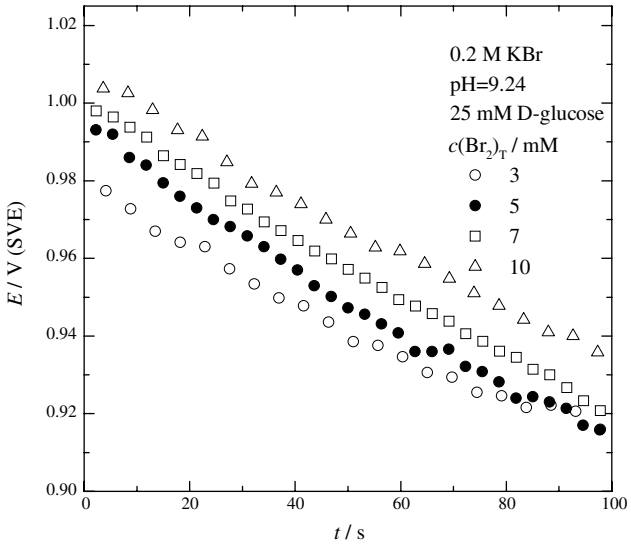

Figure 7. Time dependence of equilibrium potential for different concentrations of total bromine with constant concentration of D-glucose and bromide ions.

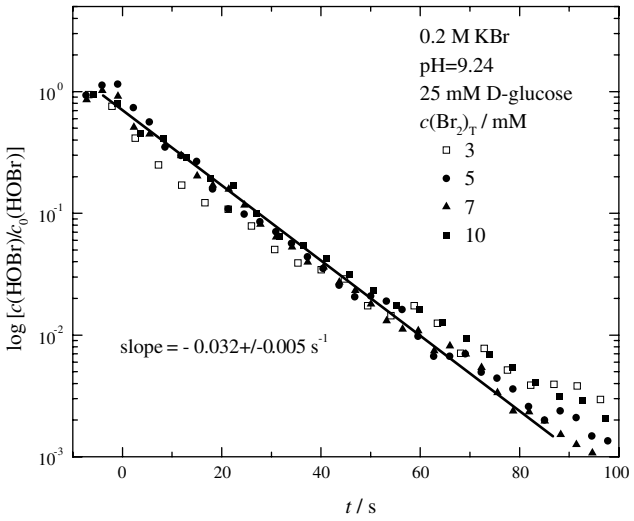

Figure 8. Time dependence of the logarithm of the ratio of actual and zero time concentration of hypobromous acid, for different total bromine concentrations.

$$\log\frac{c_0(\mathrm{HOBr})}{c(\mathrm{HOBr})}=\frac{k'}{2.303}t \tag{27a}$$

the equilibrium potential can be given as a function of reaction time as

$$E_r=E_r^{\theta}(\mathrm{HOBr}|\mathrm{Br}^-)-\frac{2.303RT}{2F}\log\frac{c(\mathrm{Br}^-)}{c_0(\mathrm{HOBr})c(\mathrm{H_3O^+})}-k'\frac{RT}{2F}t \tag{28}$$

or at constant pH

$$E_r=\mathrm{const}-k'\frac{RT}{2F}t \tag{29}$$

So, it is possible to determine the value of the rate constant from the slope of the linear part of the equilibrium potential time dependence:

$$k'=-\frac{2F}{RT}\mathrm{slope} \tag{30}$$

The constant k' is defined for constant values of bromine and bromide ions concentration at zero time by varying glucose concentration, according to

$$k'=kc^s(\mathrm{Br}^-)c^p(\mathrm{G})=k''c^p(\mathrm{G}) \tag{31}$$

Considering Eq. 30, one obtains

$$-\mathrm{slope}=\frac{RT}{2F}k''c^p(\mathrm{G}) \tag{32}$$

and by taking the logarithmic form of a rearranged Eq. 32:

$$\log(-\mathrm{slope})-\log\frac{RT}{2F}=\log k''+p\log c(\mathrm{G}) \tag{33}$$

a determination of the partial reaction order, p, for D-glucose and the rate constant, k'', is possible.

In this manner, values of equilibrium potential as a function of time were measured for different D-glucose concentrations as shown in Figure 9.

As it can be seen in Figure 9, an initial linear dependence of equilibrium potential on time is observed, and the constant k' can be calculated from the slope using Eq. 30, as shown in Table 1.

If Eqs. 31 and 33 are graphically presented, the reaction order with respect to D-glucose can be calculated from the slope, and from the intercept at a glucose concentration of 1.0 M, the value of the rate constant, k'', is obtained. These results are given in Figures 10 and 11. The reaction order determined for D-glucose by this method is 2, and the calculated second-order rate constant k'' is essentially the same, 160 $\mathrm{M^{-1}\,s^{-1}}$.

From Eq. 21, it is obvious that the value of the equilibrium potential is also dependent on the bromide ion concentration. Therefore, in order to complete the rate equation, it is necessary to determine the reaction order of bromide ion as well. In Figure 12 the equilibrium potential change as a function of time for different bromide ion concentrations is shown, while keeping the pH and total bromine concentration constant.

From Figure 12 it can be seen that for reaction times less than 20 s, the equilibrium potential value dropped

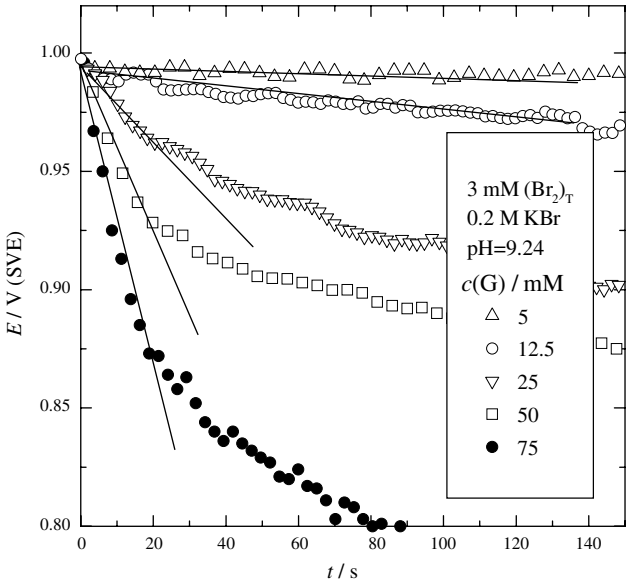

Figure 9. Time dependence of measured equilibrium potentials for different D-glucose concentrations.

Table 1. The value of the slope determined for different D-glucose concentrations (Fig. 9) for the constant concentrations of $c(\mathrm{Br_2})_T$ = 3 mM and calculated rate constant, k', using Eq. 30

c(Glucose) (M)	−Slope ($\mathrm{V\,s^{-1}}$)	k' ($\mathrm{s^{-1}}$)
0.005	2.97×10^{-5}	0.00235
0.0125	2.01×10^{-4}	0.0159
0.025	0.00121	0.0951
0.05	0.00389	0.30816
0.075	0.00716	0.56721

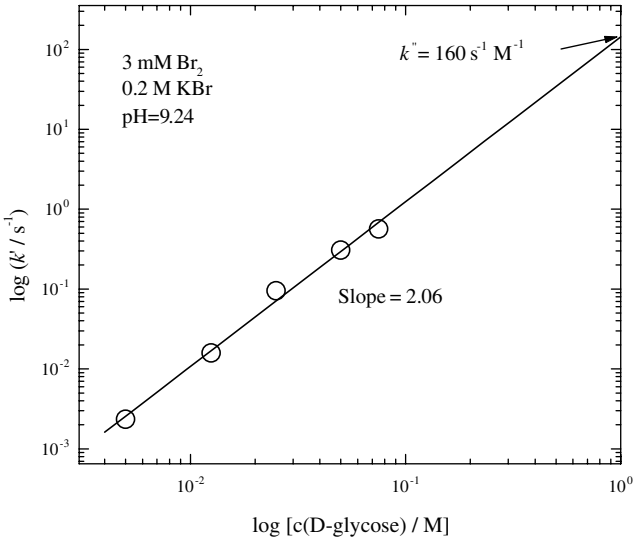

Figure 10. Graphical presentation of Eq. 31.

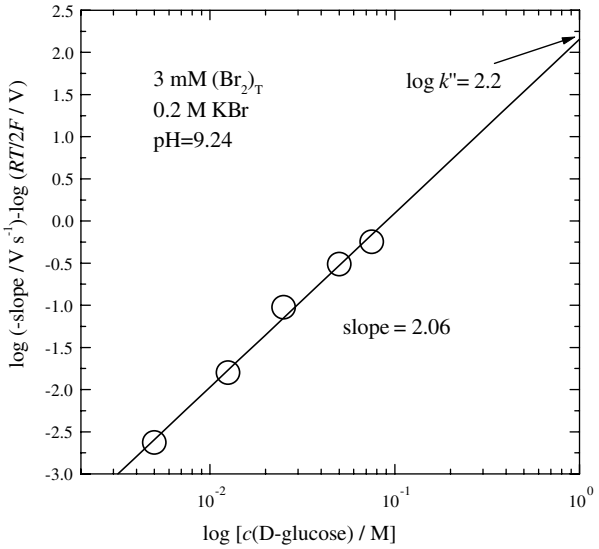

Figure 11. Graphical presentation of Eq. 33.

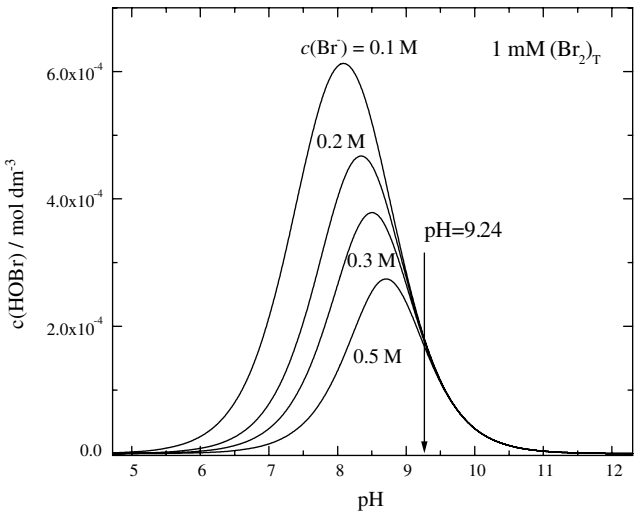

Figure 13. Distribution of hypobromous acid concentration at constant total bromine concentration of 1 mM and different bromide ion concentrations and pH values.

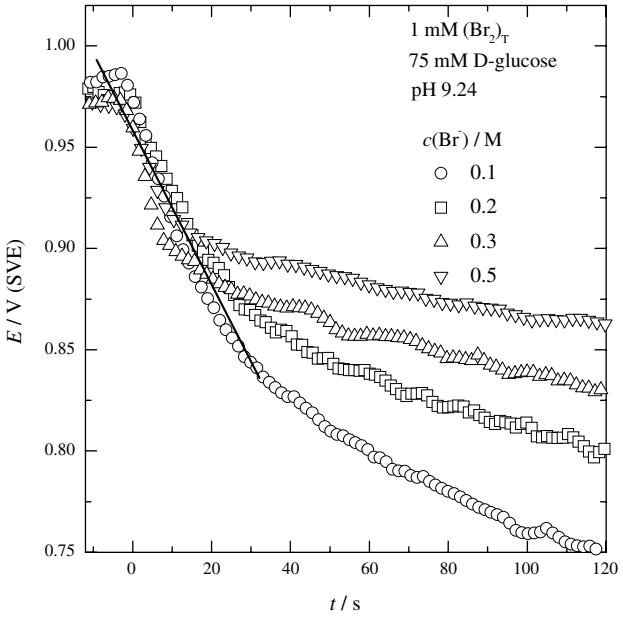

Figure 12. Time dependences of measured equilibrium potentials at constant total bromine concentration of 1 mM and different bromide concentrations.

by ~90 mV, equivalent to a decrease of the concentration of the active species by three orders of magnitude. For short reaction times, the change in bromide ion concentration has essentially no influence on the reaction rate. Therefore, it can be assumed that the reaction order with respect to bromide ion is equal to zero. For times longer than 20 s, the reaction rate decreased with increase of bromide ion concentration, which means that the reaction order is negative. However, for time greater than 20 s, the concentration of the active species could be neglected, and the reaction is determined by the kinetics of Br_2 and Br_3^- ion hydrolysis. It is surprising that the value of the reaction order of bromide ion is zero, considering that the bromide ion has great influence on the distribution of the bromine species in the solution. However, if the distribution curves for hypobromous acid are drawn, for the constant value of the bromide ion concentration, as shown in Figure 13, it is evident that at pH values greater than 9, the bromide ion concentration has no influence on the change of hypobromous acid concentration. By this, the change in reaction order of the bromide ion is explained. This also confirms that the active species in the D-glucose oxidation at the beginning of the reaction is really hypobromous acid.

Based on the parameters determined at pH 9.24, the kinetic equation for D-glucose oxidation to D-gluconate by Br_2 is therefore

$$\frac{dc(GA)}{dt} = kc^p(G)c^q(Br)c^r(H^+)c^s(Br^-) \tag{24}$$

which can be rewritten as

$$\frac{dc(GA)}{dt} = 160c^2(G)c^0(Br^-)c^0(H^+)c_0(HOBr) = 160c^2(G)c_0(HOBr) \tag{34}$$

where $c_0(HOBr)$ can be explicitly calculated by combining Eqs. 12 and 13.

The measurable equilibrium potential change as a function of time can be obtained from Eq. 28 as

$$E_r = E_r^\theta(HOBr|Br^-) - \frac{2.303RT}{2F}\log\frac{c(Br^-)}{c_0(HOBr)c(H_3O^+)} - 160\frac{RT}{2F}c^2(G)t \tag{35}$$

4. Conclusions

The kinetics of D-glucose oxidation to D-gluconic acid in aqueous solution are investigated by potentiometric technique. The reaction is strongly pH dependent, as the pH affects the bromine and bromide ion equilibrium.

At pH 9.24, kinetic parameters for the reaction were determined, assuming that the dominant active bromine species is hypobromous acid.

The kinetic parameters at this pH are as follows:

(1) The reaction order in hydrogen ion is zero.
(2) The reaction is pseudo first order in hypobromous acid, and the rate constant is 0.075 s^{-1}.
(3) The reaction is second order in D-glucose, and the determined rate constant is 160 M^{-1} s^{-1}.
(4) The reaction order in bromide ion is zero.

The kinetic equation for the formations of D-gluconic acid formation is proposed in the form

$$dc(GA)/dt = 160c^2(G)c_0(HOBr)c^0(H^+)c^0(Br^-)$$

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Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.carres.2006.04.035.

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