THE OXIDATION OF D-GLUCOSE AND D-FRUCTOSE WITH OXYGEN IN AQUEOUS, ALKALINE SOLUTIONS

PART II. THE OVERALL KINETICS

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(Received August 5th, 1971; accept for publication in revised form, December 16th, 1971)

ABSTRACT

Based on a previously reported, integral reaction-scheme, a very simple, kinetic model for the homogeneous oxidation of D-glucose and D-fructose in aqueous, alkaline solutions has been developed. It involves the influence of the type and concentration of the hexose, the hydroxyl-ion concentration, the oxygen concentration in the liquid phase, and the temperature on the rate of formation of the acidic reaction products. No attention is paid to the product distribution.

INTRODUCTION

In a previous paper[1]†, an integral reaction scheme for the oxidation of D-glucose and D-fructose with oxygen in aqueous, alkaline solutions was developed. Basically, the process involves a rapid de-protonation of the D-glucose molecules, followed by development of an enolate ion structure. From the initially formed enolate ions, in addition to the formation of fructose, a great number of other kinds of enolate ions may arise which are oxidised to peroxides. Acidic products are then formed from the peroxides.

From the integral reaction scheme, it appears that, in general, two acids are formed from each enolate ion. Because ~2.5 acidic functions are formed per hexose molecule that has been converted, an average number of 1.25 enolate ions are formed per enolate ion E_{61}^-.

For the purpose of describing the influence of the type and concentration of the hexose, the hydroxyl concentration, the oxygen concentration in the liquid phase, and the temperature on the overall production rate of acids, the integral scheme could be simplified. The attainment of equilibrium between E^- and P^- is described as an overall, irreversible reaction, which is controlled by one effective rate constant. The

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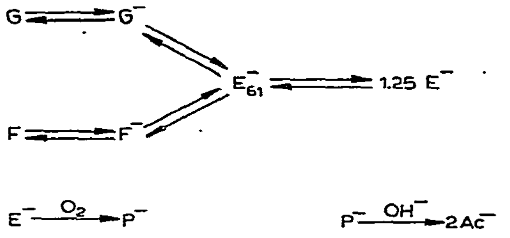
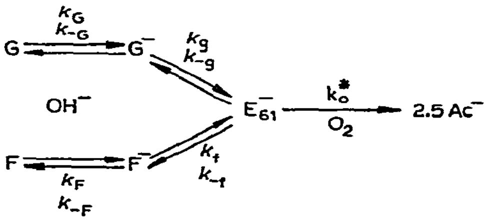
†This paper includes a description of the apparatus, experimental and analytical procedures, and process parameters, and an explanation of symbols.

influence of the process parameters on the product distribution is not built into the scheme, because no attention is paid to the internal distribution of the various enolate ions, nor to the hypothetical influence of the hydroxyl ion on the formation of acidic products *via* a double negative peroxide[1].

A kinetic model



The above model can be further simplified by the following considerations: (*a*) because the product distribution is independent of the reaction time, the ratio $(E^-)/(E_{61}^-)$ must be constant during the reaction; (*b*) from peroxide analysis, a maximal concentration $(P^-) = 0.005$ was found, and so the two irreversible, consecutive reactions can be combined. The resulting, overall, kinetic model is therefore as follows:



Basic equations

The following basic equations are associated with the model:

$$\frac{d(G)}{dt} = -k_G(G)[OH] + k_{-G}(G^-) \tag{1}$$

$$\frac{d(G^-)}{dt} = -k_G(G^-) - k_g(G^-) + k_G(G)[OH] + k_{-g}(E_{61}^-) \tag{2}$$

$$\frac{d(F)}{dt} = -k_F(F)[OH] + k_{-F}(F^-) \tag{3}$$

$$\frac{d(F^-)}{dt} = k_{-F}(F^-) - k_f(F^-) + k_F(F)[OH] + k_{-f}(E_{61}^-) \tag{4}$$

$$\frac{d(E_{61}^{-})}{dt} = k_g(G^-)-k_{-g}(E_{61}^{-})+k_f(F^-)-k_{-f}(E_{61}^{-})-k_o^*[O_1](E_{61}^{-}) \qquad (5)$$

$$\frac{d(Ac^-)}{dt} = 2.5k_o^*[O_1](E_{61}^{-}) \qquad (6)$$

Equation *6* represents the oxygen consumption rate: d(TOC)/dt. (*7*)

The equilibria $G \rightleftarrows G^-$ and $F \rightleftarrows F^-$ are attained instantaneously, so that the absolute values of the reaction rate constants k_G, k_{-G}, k_F, and k_{-F} are not relevant and can be replaced by the respective ionisation constants K_G and K_F.

$$K_G = \frac{k_G}{k_{-G}} = \frac{(G^-)}{(G)[OH]} \qquad (8)$$

$$K_F = \frac{k_F}{k_{-F}} = \frac{(F^-)}{(F)[OH]} \qquad (9)$$

In order to explain the experimentally observed, higher reactivity of fructose with respect to glucose, the attainment of the equilibrium $F^- \rightleftarrows E_{61}^-$ must be more rapid than the conversion $G^- \rightleftarrows E_{61}^-$. For this reason, it is assumed that, during our analytical procedure[2], as a result of the acidic treatment of the samples, the reactions $G^- \rightarrow G$, $E^- \rightarrow E_{61}^- \rightarrow F^- \rightarrow F$ occur. Consequently, the analytically determined concentration of, for example, D-glucose is

$$(G)^a = (G)+(G^-) \qquad (10)$$

and

$$(F)^a = (F)+(F^-)+(E^-) \qquad (11)$$

From equations *8* and *10*, it follows that

$$(G^-) = \frac{K_G[OH]}{K_G[OH]+1}(G)^a, \qquad (12)$$

and from equations *9* and *11*, it follows that

$$(F^-) = \frac{K_F\,[OH]}{K_F\,[OH]+1}\{(F)^a-(E^-)\}. \qquad (13)$$

For each moment during the reaction, the following mass-balances can be calculated:

$$TAC = (G^-)+(F^-)+(E^-)+(P^-)+(Ac^-) \qquad (14)$$

$$TOC = (Ac^-)+2(P^-) \qquad (15)$$

If the above-mentioned peroxide concentration is neglected, it follows, from equations *14* and *15*, that

$$\mathrm{TAC}-\mathrm{TOC} = (\mathrm{G}^-)+(\mathrm{F}^-)+(\mathrm{E}^-) \qquad (16)$$

Combination of equations *12*, *13*, and *16* leads to

$$(\mathrm{E}^-) = \left[\mathrm{TAC}-\mathrm{TOC}-\frac{\mathrm{K_G[OH]}}{\mathrm{K_G[OH]}+1}\times(\mathrm{G})^{\mathrm{a}}-\frac{\mathrm{K_F[OH]}}{\mathrm{K_F[OH]}+1}\times(\mathrm{F})^{\mathrm{a}}\right]\times$$

$$\times\ [\mathrm{K_F[OH]}+1] \qquad (17)$$

(E^-) was calculated for a number of experiments with different [OH] and $[\mathrm{O}_1]$. The numerical value of (E^-) always varied arbitrarily around zero as a function of the reaction time, within the inaccuracy range of our analytical method. It was therefore concluded that the total enolate concentration was always very low with regard to $(\mathrm{F})^{\mathrm{a}}$.

As the result of the above considerations, equations *1–4* can be replaced by:

$$\frac{\mathrm{d(G)^a}}{\mathrm{dt}} = -k_{\mathrm{g}}(\mathrm{G}^-)+k_{-\mathrm{g}}(\mathrm{E}_{61}^-) \quad (18),\ \text{and}\ \frac{\mathrm{d(F)^a}}{\mathrm{dt}} = -k_{\mathrm{f}}(\mathrm{F}^-)+k_{-\mathrm{f}}(\mathrm{E}_{61}^-) \quad (19),$$

$$\text{in which } (\mathrm{G}^-) = \frac{\mathrm{K_G[OH]}}{\mathrm{K_G[OH]}+1}(\mathrm{G})^{\mathrm{a}} \quad (20),\ (\mathrm{F}^-) = \frac{\mathrm{K_F[OH]}}{\mathrm{K_F[OH]}+1}(\mathrm{F})^{\mathrm{a}} \quad (21),$$

$$\text{and from equation 7 } (\mathrm{E}_{61}^-) = \frac{1}{2.5k_{\mathrm{o}}^*[\mathrm{O}_1]}\cdot\frac{\mathrm{d(TOC)}}{\mathrm{dt}} \quad (22).$$

Values of $\mathrm{K_G}$ and $\mathrm{K_F}$, calculated from titration curves of D-glucose and D-fructose, are as follows:

K (l/mmole)	*25°*	*45°*	*50°*	*55°*	*60°*	*65°*	*E (kcal/mole)*
$\mathrm{K_G}\times10^3$	31	20	18	16	15	14	−4.0
$\mathrm{K_F}\times10^3$	49	29	26	23	20	18	−5.3

Our data are in good agreement with those found by Izatt *et al.*[4]: $\mathrm{K_G}$ (25°) = 31×10^{-3} and $\mathrm{K_F}$ (25°) = 54×10^{-3}.

Determination of the reaction rate constants

Because the real, absolute value of (E_{61}^-) could not be determined as a function of time, it is only possible to calculate k_{g} and k_{f}, and the mutual relations between $k_{-\mathrm{g}}$, $k_{-\mathrm{f}}$, and k_{o}^*. In order to simplify the following equations, we introduce

$$\mathrm{X} = \frac{\mathrm{K_G[OH]}}{\mathrm{K_G[OH]}+1},\quad \mathrm{Y} = \frac{\mathrm{K_F[OH]}}{\mathrm{K_F[OH]}+1},\quad \text{and } \mathrm{Z} = \frac{1}{2.5[\mathrm{O}_1]}.$$

Substitution of equations *20* and *22* into *18* gives

$$\frac{d(G)^a}{dt} = -k_g.X.(G)^a + \frac{k_{-g}}{k_o^*}.Z.\frac{d(TOC)}{dt}. \qquad (23)$$

Substitution of equations *21* and *22* into *19* gives

$$\frac{d(F)^a}{dt} = -k_f.Y.(F)^a + \frac{k_{-f}}{k_o^*}.Z.\frac{d(TOC)}{dt}. \qquad (24)$$

For each experiment, X, Y, and Z can be calculated, because [OH], $[O_1]$, and the reaction temperature are known. The values of K_G and K_F are given above. At any time during an experiment, $(G)^a$, $(F)^a$, and TOC are known, and consequently their first derivatives versus time. So the unknown rate constants k_g, k_f, k_{-g}/k_o^*, and k_{-f}/k_o^* can be solved from equations *23* and *24*, either analytically or graphically. The last method is illustrated in Fig. 1, which has been calculated from the data of a D-fructose oxidation experiment (experiment code B in ref. 1).

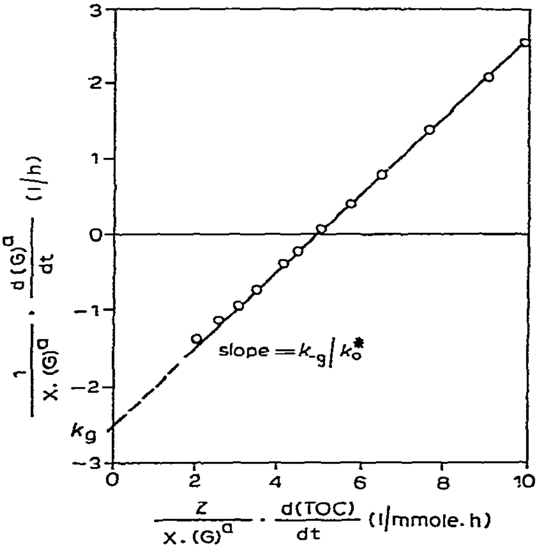


Fig. 1. The determination of k_g and k_{-g}/k_o^* for D-fructose oxidation: $[F]_0 = 215$, $[OH] = 26$, and $[O_1] = 0.85$ mmoles/l; T = 50°.

RESULTS AND DISCUSSION

In principle, the values of k_g, k_f, k_{-g}/k_o^*, and k_{-f}/k_o^* can be determined from each separate experiment. However some difficulties arise. (*a*) The same value of k_g was obtained from experiments that started with D-glucose or D-fructose. However, the value of k_{-g}/k_o^* appeared to be higher by a factor of 1.5 if the experiment was started with D-glucose instead of D-fructose. This phenomenon is related to neglect of the distinction between α and β anomers in the model. (*b*) The determination of k_f and k_{-f}/k_o^* was complicated by a less-accurate analysis of D-fructose, probably due to anhydride formation during our analytical procedure[2]. Furthermore, the comment (*a*) applies also to D-fructose.

The results of our calculations are listed in Table I.

TABLE I

NUMERICAL VALUES OF REACTION RATE-CONSTANTS

Temperature (degrees)	k_g *l/h*	k_f *l/h*	k_{-g}/k_o^* *mmoles/l*	k_{-f}/k_o^* *mmoles/l*
50	2.5 ±0.2	12 ±3	0.8 ±0.3	5 ±3
60	15 ±2	50 ±10	1.4 ±0.3	7 ±3

In order to check the validity of our simplified kinetic model, it has been simulated on an analogue computer. The results of a given glucose oxidation experiment are represented in Fig. 2. It follows that the agreement between the calculated and observed curves is only good for approximately the first 50% of glucose conversion. The similarity between the two sets of curves becomes much better when a distinction

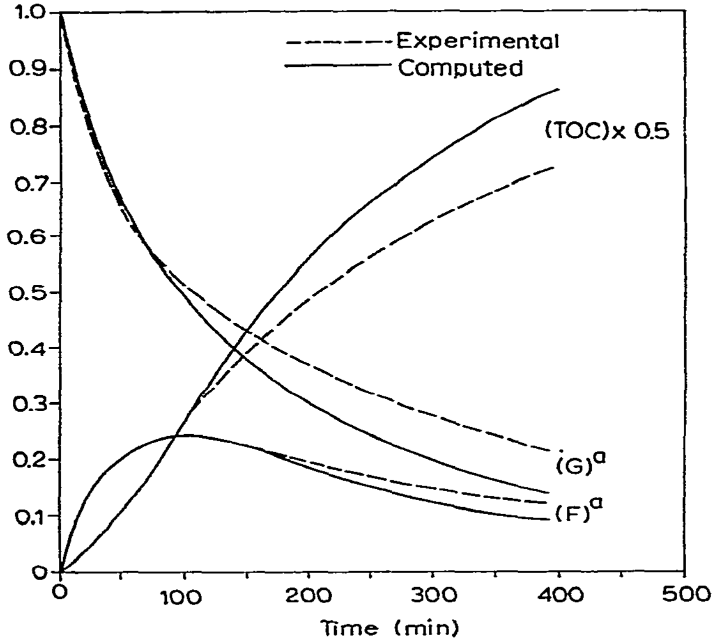


Fig. 2. Comparison between experimental and computed results for D-glucose oxidation: $[G]_o = 215$, $[OH] = 26$, and $[O_l] = 0.85$ mmoles/l; T = 50°. Rate constants: $K_G = 18.10^{-3}$, $K_F = 26.10^{-3}$ l/mmole; $k_g = 2.5$, $k_f = 12$ l/h; $k_{-g}/k_o^* = 0.7$, $k_{-f}/k_o^* = 6.0$ mmoles/l.

between α- and β-D-glucose anomers is introduced. In Fig. 3, the ratio $(\beta G)^a/(\alpha G)^a$ versus the oxygen consumption has been plotted for a number of experiments with different process conditions.

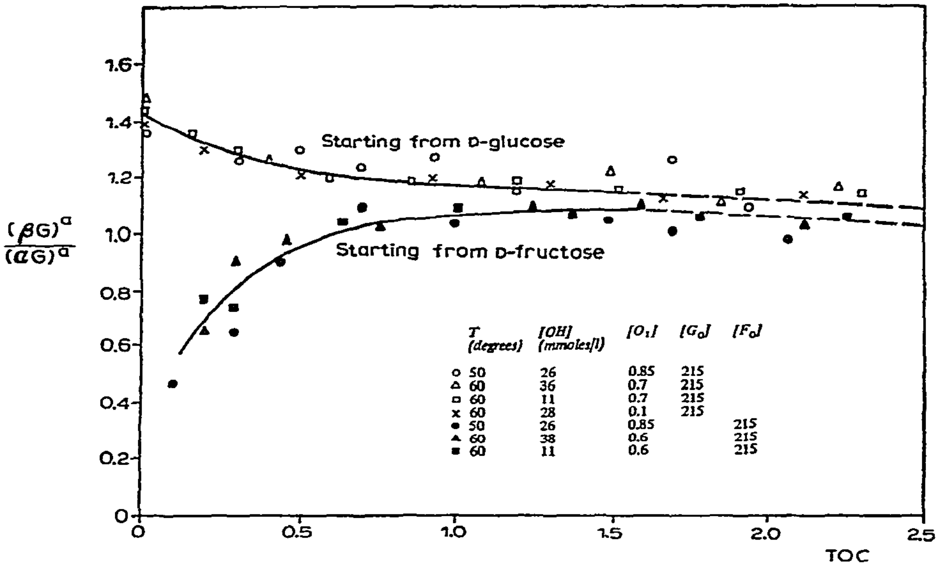
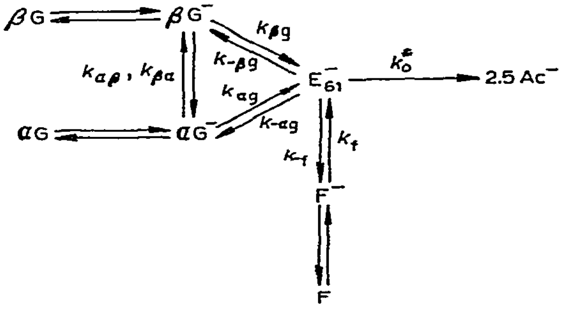


Fig. 3. The ratio $(\beta G)^a/(\alpha G)^a$ plotted as a function of the course of the reaction (TOC) for D-glucose and D-fructose oxidation experiments.

Fig. 3 can be qualitativily explained by the following adjustment of the kinetic model.



Because of a higher reactivity of βG with respect to αG, the initial ratio $(\beta G)^a/(\alpha G)^a$ in a D-glucose oxidation experiment decreases during the course of the reaction. However, a pseudo equilibrium between βG and αG will be reached due to direct ($k_{\beta\alpha}$ and $k_{\alpha\beta}$) and indirect (*via* E_{61}^-) interconversion routes between the two anomers.

When it is assumed that the ionisation constants for αG and βG are the same, the rate equation *23* changes into:

$$\frac{d(G)^a}{dt} = -k_{\alpha g}.X.(\alpha G)^a - k_{\beta g}.X.(\beta G)^a + \frac{k_{-\beta g}+k_{-\alpha g}}{k_o^*}.Z.\frac{d(TOC)}{dt}. \qquad (25)$$

From equation *25*, it follows that the rate of disappearance of D-glucose depends not only on the total D-glucose concentration $(G)^a = (\alpha G)^a + (\beta G)^a$, but also on the actual ratio $(\beta G)^a/(\alpha G)^a$. Consequently, $-d(G)^a/dt$ will decrease more rapidly as a function of the conversion according to equation *23*, because of a decreasing ratio $(\beta G)^a/(\alpha G)^a$ during the reaction.

By analogue simulation, the validity of the above model has been checked, starting with the *k*-values of the simpler model (Fig. 2) extended with the following assumptions.

(*a*) $k_{-\alpha g} = 2k_{-\beta g}$. This relationship can be derived from the observed, initial ratio $(\beta G)^a/(\alpha G)^a = 0.5$ in the D-fructose oxidation experiments (Fig. 3).

(*b*) $k_{\alpha g} = 0.5k_{\beta g}$. This relationship has been concluded from the relative, initial reaction-rates from two experiments with, respectivily, almost pure α and β forms of D-glucose. Kinetically, this statement, combined with the earlier assumption that the ionisation constants of α- and β-D-glucose are the same, is equivalent to the introduction of different ionisation constants $K_{\alpha G} = 0.5K_{\beta G}{}^5$, and $k_{\alpha g} = k_{\beta g}$.

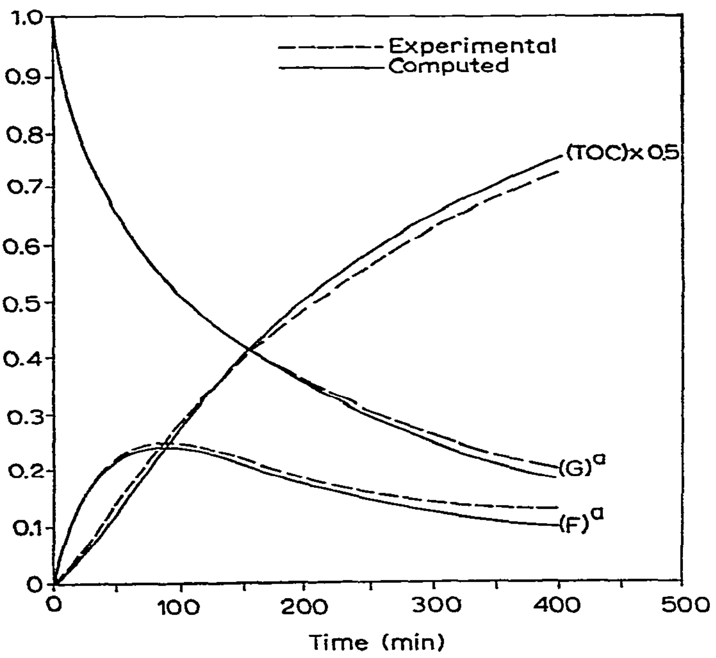


Fig. 4. Comparison between experimental and computed results experiment (see Fig. 2). Rate constants: $K_G = 18.10^{-3}$, $K_F = 26.10^{-3}$ l/mmole; $k_{\alpha g} = 1.6$, $k_{\beta g} = 3.2$, $k_f = 12$ l/h; $k_{-\alpha g}/k_o^* = 1.8$, $k_{-\beta g}/k_o^* = 0.9$, $k_{-f}/k_o^* = 6$ mmoles/l; $k_{\alpha\beta} = 1.2$, $k_{\beta\alpha} = 3.6$ l/h. $(\beta G)^a/(\alpha G)^a = 1.5$ at $t = 0$.

In Fig. 4, the result of our analogue simulation of the adjusted kinetic model is illustrated. With the given set of *k*-values, the best correspondence between calculated and observed $(G)^a$, $(F)^a$, TOC, and $(\beta G)^a/(\alpha G)^a$ versus time curves has been obtained for both the D-glucose and D-fructose oxidation experiments.

Although the present kinetic model is a gross simplification, we have found that it fits, with reasonable accuracy, the oxidative degradation of D-glucose and D-fructose within the studied range of parameters.

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