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

PART III.* A KINETIC APPROACH TO THE PRODUCT DISTRIBUTION

H. G. J. DE WILT AND B. F. M. KUSTER
Department of Chemical Engineering, University of Technology, Eindhoven (The Netherlands)

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ABSTRACT

Based on a previously reported, integral reaction-scheme for the homogeneous oxidation of D-glucose and D-fructose with oxygen in aqueous, alkaline solutions, a kinetic model covering the product distribution has been developed. The model consists of a repeated set of reactions with constant rate coefficients, starting from each enolate ion. The product distribution can be understood as a function of the temperature, the hydroxyl-ion concentration, and the oxygen concentration in the liquid phase.

INTRODUCTION

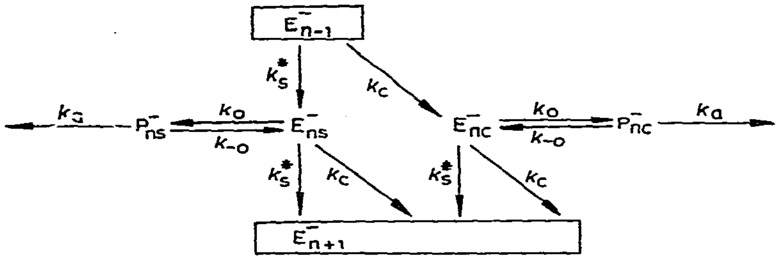
In a previous paper[1]*, an integral reaction scheme for the oxidation of D-glucose and D-fructose with oxygen in aqueous, alkaline solutions was developed. The preceding paper[2] deals with the overall kinetics of the reaction and describes the influence of the type and concentration of the hexose, the hydroxyl-ion concentration, the oxygen concentration in the liquid phase, and the temperature on the rate of the total acid production. The influence of these parameters on the product distribution is the subject of the present paper.

From the integral scheme, it follows that the product distribution depends on the subdivision within the total number of enolate ions. Basically, each type of enolate ion can give both a peroxide and other enolate ions, which can be schematically represented by means of a division of the enolate ions into classes. In this division, E_n^- includes all the enolate ions and equivalent aldehydes which are formed by way of (n−1) steps starting from E_{61}^- (where the subscripts 6 and 1 refer to the length of the carbon chain and the position of the double bond, respectively): $\rightarrow E_{n-1}^- \rightarrow E_n^- \rightarrow E_{n+1}^- \rightarrow$ etc. Thus, class E_1^- includes E_{61}^-, E_2^- includes $E_{62}^- + E_{31}^-$ + GyA, E_3^- includes $E_{63}^- + E_{42}^-$ + GoA, E_4^- includes E_{52}^- + FoA + E_{41}^-, etc.

Part II: preceding paper[2].

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

The actual concentration of a particular ion is presumed to decrease when the number of the class to which it belongs increases. The reactions which are related to the ions of a given class are illustrated in the following scheme.



In contrast to the overall kinetic model (Part II[2]), the equilibrium between E^- and P^- had to be included here in order to explain the influence of the hydroxyl-ion concentration on the product distribution. The attainment of the equilibrium $E_n^- \rightleftarrows E_{n-1}^-$ *via* double-bond shift is described as an irreversible reaction which is controlled by an effective rate constant k_s^*. The irreversible cleavage of E^- is represented by k_c; E_n^- is formed from E_{n-1}^- either by double-bond shift or by cleavage, denoted by E_{ns}^- and E_{nc}^-, respectively; k_s^* and k_c are supposed to be constant for all transfers from a lower class to a higher one; k_o and k_{-o} are supposed to be constant for all oxidation steps. From our previous papers[1,2], it is known that the product distribution is independent of the reaction time and that the total enolate ion and peroxide concentrations are very low. A steady-state concept for (E_n^-) and (P_n^-) can therefore be used.

Basic equations

$$\frac{d(P_{ns,c}^-)}{dt} = 0 = k_o[O_1](E_{ns,c}^-)-(k_{-o}+k_a[OH])(P_{ns,c}^-) \tag{1}$$

$$\frac{d(E_{ns}^-)}{dt} = 0 = k_s^*(E_{n-1}^-)-(k_o[O_1]+k_s^*+k_c)(E_{ns}^-)+k_{-o}(P_{ns}^-) \tag{2}$$

$$\frac{d(E_{nc}^-)}{dt} = 0 = k_c(E_{n-1}^-)-(k_o[O_1]+k_s^*+k_c)(E_{nc}^-)+k_{-o}(P_{nc}^-) \tag{3}$$

From equation *1*, it follows that

$$(P_{ns,c}) = \frac{k_o[O_1]}{k_{-o}+k_o[OH]}\cdot(E_{ns,c}^-). \tag{4}$$

After defining $\alpha=(E_{ns}^-)/(E_{n-1}^-)$ and $\beta=(E_{nc}^-)/(E_{n-1}^-)$, substitution of equation *4* into *2* gives

$$\alpha = \frac{(k_s^*k_{-o}/k_ak_o) + k_s^*[OH]/k_o}{[O_1][OH]+[(k_c+k_s^*)/k_s\times(k_s^*k_{-o}/k_ak_o)]+k_s^*[OH]/k_o} \tag{5}$$

Substitution of equation *4* into *3* leads to

$$\beta = \frac{k_c k_{-o}/k_a k_o + k_c[\mathrm{OH}]/k_o}{[\mathrm{O}_1][\mathrm{OH}] + [(k_c+k_s^*)/k_c \times k_c k_{-o}/k_a k_o] + k_c[\mathrm{OH}]/k_o} \tag{6}$$

From equations *5* and *6*, it follows that $\frac{\alpha}{\beta} = \frac{(\mathrm{E}_{\mathrm{ns}}^-)}{(\mathrm{E}_{\mathrm{nc}}^-)} = \frac{k_s^*}{k_c}$ *(7)*

which is a logical consequence of our propositions.

If the concentration of D-arabinonic acid (Ar) is given a normalised value 1, because it is formed directly from E_{61}^-, the concentration of each product can be expressed relative to that of D-arabinonic acid in terms of α and β. From the integral reaction scheme[1], it follows that, for D-erythronic acid (Er), $(\mathrm{Er})/(\mathrm{Ar}) = \alpha + \alpha^3\beta$, because the production of D-erythronic acid is proportional to the concentration of E_{62}^- and E_{51}^-.

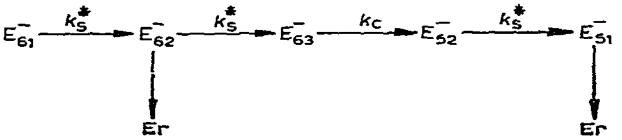


Table I lists the corresponding expressions for all of the acids formed.

TABLE I

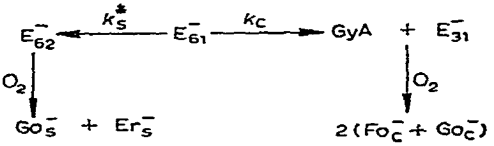
PRODUCT CONCENTRATIONS (*i*) RELATIVE TO D-ARABINONIC ACID[a]

Product	(i)/(*Ar*)
Arabinonic acid (Ar)	1
Erythronic acid (Er)	$\alpha+\alpha^3\beta$
Glyceric acid (Gy)	$2\alpha^2+2\alpha^2\beta+\alpha^3\beta^2$
Glycolic acid (Go)	$\alpha+2\beta+3\alpha\beta+\alpha^2\beta+3\alpha^2\beta^2+2\alpha^3\beta^2+\alpha^3\beta^3$
Formic acid (Fo)	$1+2\beta+2\alpha^2\beta+3\alpha^2\beta^2+\alpha^3\beta+2\alpha^3\beta^2+2\alpha^3\beta^3$
Total acid (Ac)	$2+2\alpha+4\beta+3\alpha\beta+5\alpha^2\beta+6\alpha^2\beta^2+2\alpha^3\beta+5\alpha^3\beta^2+3\alpha^3\beta^3$

[a] The product concentration relative to the total acid concentration can be obtained by multiplying with (Ar)/(Ac).

An estimation of $\alpha/\beta = k_s^*/k_c$

Starting from experimentally determined product concentrations, an estimate of the ratio α/β can be made with the aid of a simplified part of the integral reaction scheme, starting from E_{61}^-.



According to this scheme, the value of $\alpha/\beta = k_s^*/k_c$ can be estimated by calculating, from experimental data, the ratio of the normalised concentrations of glycolic acid, formed either by double-bond shift or by cleavage. It follows from the scheme that $(\mathrm{Er}^-) = (\mathrm{Er}_s^-)$, $(\mathrm{Go}^-) = (\mathrm{Go}_s^-) + (\mathrm{Go}_c^-)$, and $(\mathrm{Go}_s^-) = (\mathrm{Er}_s^-)$. Therefore,

$$\alpha/\beta = \frac{(\mathrm{Go}_s^-)}{0.5(\mathrm{Go}_c^-)} = \frac{(\mathrm{Er}^-)}{0.5(\mathrm{Go}^-) - 0.5(\mathrm{Er}^-)}.$$

The value of α/β obtained in this way is only an approximation because, in the above, partial scheme, the formation of glycolic acid by repeated double-bond shift and cleavage of E_{62}^- has been neglected. From a number of experiments with different process conditions, we found average α/β values of 4 at 50° and 3 at 60°.

After substituting for α and β in the equations of Table I, a theoretical product concentration relative to the total acid concentration was calculated as a function of α at 50 and 60°. The resulting curves at 50° are represented in Fig. 1.

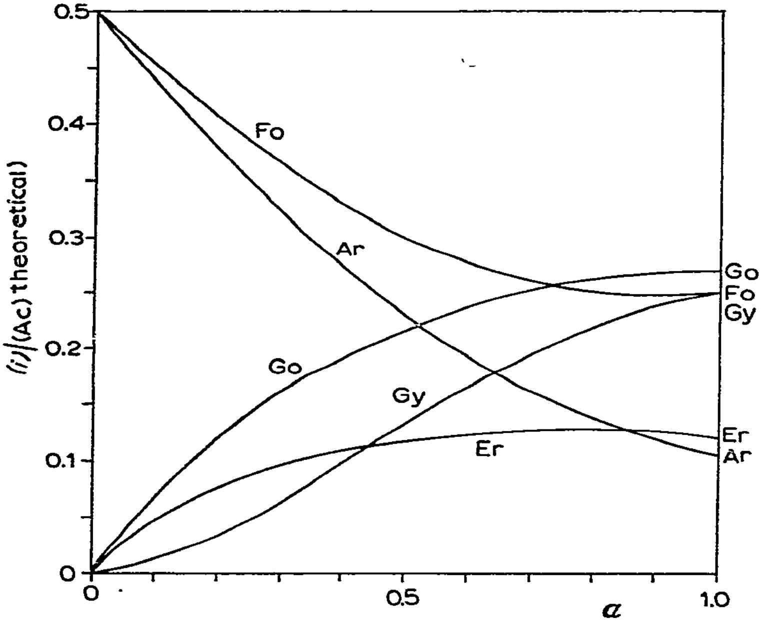


Fig. 1. The calculated, theoretical, product distribution as a function of α.

The product concentrations measured in each experiment can be compared with the theoretical ones as a function of α. The deviation between the measured and theoretical value for a given product is denoted by Δ_i. By means of minimalisation of $\Sigma\Delta_i$ as a function of α, the most suitable value of α for each experiment can be determined accurately as shown in Fig. 2.

TABLE II

COMPARISON BETWEEN CALCULATED AND MEASURED PRODUCT DISTRIBUTIONS

Initial[a] *hexose*	$[OH]$ *mmoles/l*	$[O_1]$	*T*	α	$(Ar)/(Ac)$[b]		$(Er)/(Ac)$[b]		$(Gy)/(Ac)$[b]		$(Go)/(Ac)$[b]		$(Fo)/(Ac)$[b]	
			(degrees)		*Calc.*	*Obs.*	*Calc.*	*Obs.*	*Calc.*	*Obs.*	*Calc.*	*Obs.*	*Calc.*	*Obs.*
G	26	0.85	50	0.40	26	26	11	11	10	10	20	19	33	33
F	26	0.85	50	0.40	24	26	13	11	10	10	21	19	32	33
F	31	0.2	50	0.82	12	13	12	13	21	22	25	24	30	26
G	36	0.7	60	0.48	21	22	11	11	13	12	24	23	31	31
G	11	0.7	60	0.61	19	18	11	12	14	16	27	26	29	29
F	38	0.7	60	0.52	19	20	12	11	14	13	24	24	31	31
F	11	0.6	60	0.62	17	17	11	12	17	16	25	26	30	29
G	700	0.6	60	0.38	25	26	6	10	9	9	22	21	36	34
G	27	0.3	60	0.62	15	17	11	12	15	16	29	26	30	29
G	28	0.1	60	0.70	11	14	10	12	16	18	30	28	33	29
Correlation coefficients														
			50		0.99				1.00		0.98		0.81	
			60		0.98				0.93		0.90		0.67	

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[a] Initial hexose concentration, 215 mmoles/l; G, D-glucose; F, D-fructose. [b] $\times 10^2$.

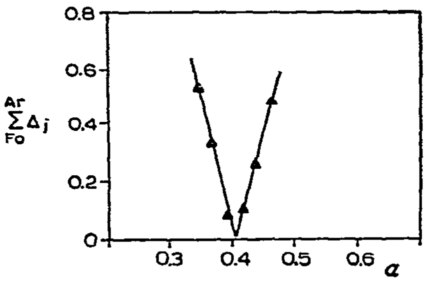

Fig. 2. The determination of α for a given experiment by minimalisation of the difference between the measured and theoretical product distribution. For oxidation of D-glucose: $[G]_o = 215$, $[OH] = 26$, and $[O_l] = 0.85$ mmoles/l. T = 50°.

Determination of k_a/k_{-o} *and* k_o/k_s^*

For each experiment, the hydroxyl-ion concentration, the oxygen concentration in the liquid phase, the value of α as determined by the above procedure, and the estimated value of $\alpha/\beta = k_s^*/k_c$ at the desired temperature were substituted into equation 5. This provided a number of independent equations with 2 variables, namely $k_{-o} \cdot k_s^*/k_a \cdot k_o$ and k_s^*/k_o. By means of the method of least squares, the set of equations was solved. The results were as follows.

Temperature (degrees)	k_c/k_s^*	k_s^*/k_o *(mmoles/l)*	k_{-o}/k_a *(mmoles/l)*
50	0.24 ±0.02	0.40 ±0.08	16 ±5
60	0.33 ±0.06	0.5 ±0.1	25 ±10

A final check was carried out by the following procedure. For a number of experiments with different process conditions, α was determined by means of equation 5 and the data in the above table. By substituting the resulting values of α in the equations in Table I, product distributions were calculated, which could be compared with the experimental data. This comparison is shown in Table II.

CONCLUSION

The product distribution can be explained by a simplified reaction scheme, consisting of a repeated set of reactions with constant rate coefficients, starting from each enolate ion. By means of the ratios of the reaction rate constants for peroxide formation, cleavage of the enolate ion, and double-bond shift within an enolate ion as given in the above table, the product distribution as a function of the temperature, the hydroxyl-ion concentration, and the oxygen concentration in the liquid phase can be predicted.

REFERENCES

1 H. G. J. DE WILT AND B. F. M. KUSTER, *Carbohyd. Res.*, 19 (1971) 5.
2 H. G. J. DE WILT AND I. LINDHOUT, *Carbohyd. Res.*, 23 (1972) 333.