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Note

Isomerization of D-glucose with sodium aluminate: kinetics as a function of temperature

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A mechanism for the isomerization of D-glucose to D-fructose was postulated in the preceding article[1]. The mechanism was based on an α-D-glucopyranose–1,2-aluminate complex that isomerized selectively to a β-D-fructofuranose–1,3,6-aluminate complex through an enol intermediate that inhibited formation of D-mannose–aluminate complexes. The D-fructose complex could then react further to give a complex of D-psicose.

The kinetics of this reaction could be of considerable commercial significance, as high yields of D-fructose approaching 60–70% can be obtained. Several questions, however, must be examined before commercial success can be realized. This paper* deals with some of these questions, including product distribution as a function of time and temperature.

DISCUSSION OF RESULTS

The mechanism discussed in the preceding paper[1] was used used as the basis for the rate model. The technique for determining the rate constants involved an optimization, least-squares, curve fit of experimental time–concentration data. The advantage of this procedure over other methods[2,3] is that equilibrium data and quantities of sometimes rare chemicals (in this case D-psicose) are not needed.

Batch reactions were conducted at various temperatures and ratios of sodium aluminate to initial concentrations of sugar. These conditions are summarized in Table I. The concentration–time data was analyzed by the mathematical technique discussed here, using the reaction scheme shown in ref. 1, Fig. 3. A typical fit of data is shown in Fig. 1. The points are experimental data, and the solid lines represent the curve defined by the computed rate-constants. The specific rate-constants corresponding to Fig. 1 are listed as run number 5 in Table II. Table II summarizes the results from all the batch reactions.

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*Taken mainly from the Ph D. Thesis of Arthur J. Shaw III, Purdue University, December, 1976.

TABLE I

SUMMARY OF CONDITIONS OF RUNS 1 THROUGH 14

Run no.	*Temp.* (°C)	*Initial g of sugar added*			*2-Hydroxy pyridine added*	*Average pH*	*Acetic acid added*	*NaOH added (amount)*	$Al(OH)_4^-$ G_0 *(molar ratio)*
		D-*Glucose*	D-*Fructose*	D-*Mannose*					
12	59.5 ± 0.1	27.5			No	11.1	No	No	1.42
11	59.5 ± 0.1	27.5			No	10.5	No	No	0.95
13	59.5 ± 0.1		27.5		No	11.2	No	No	1.42
14	59.5 ± 0.1			27.5	No	11.2	No	No	1.42
6	43.0 ± 0.5	27.5			No	11.9	No	Yes	1.00
5	43.0 ± 0.5	27.5			No	11.9	No	Yes	1.00
3	43.0 ± 0.5	27.5			No	11.6	Yes	Yes	0.95
4	43.0 ± 0.5	27.5			No	11.4	Yes	Yes	0.95
1	42.6 ± 0.5	27.5			No	11.9	No	Yes	0.95
2	42.6 ± 0.5	27.5			No	12.4	No	Yes	1.42
7	30.0 ± 0.1	27.5			No	12.4	No	No	1.42
8	30.0 ± 0.1	27.5			Yes (1 %)	12.4	No	No	1.42
10	14.5 ± 0.1	27.5			No	13.5	No	Yes (81 %)	1.42
9	14.5 ± 0.1	27.5			No	12.9	No	No	1.42

TABLE II

SUMMARY OF SPECIFIC RATE-CONSTANTS FOR THE ISOMERIZATION OF D-GLUCOSE WITH SODIUM ALUMINATE

Run ID	*Temp.* *(°C)*	*Ratio of* $Al(OH)_4^-$ *to* G_0	*Specific rate constants* (h^{-1}) k_1 G→F	k_2 F→G	k_3 F→P	k_4 P→D	k_5 F→D	k_6 G→D
12	59.5 ± 0.1	1.42	2.06	0.207	0.059	0.12	0.198	0.36
11	59.5 ± 0.1	0.95	1.17	0.196	0.065	0.22	0.109	0.29
13	59.5 ± 0.1	1.42	2.06	0.181	0.048	0.094	0.202	0.0003
6	43.0 ± 0.5	1.00	0.240	0.023	0.0070	0.016	0.0207	0.049
5	43.0 ± 0.5	1.00	0.231	0.020	0.0057	0.005	0.0206	0.024
3	43.0 ± 0.5	.95	0.160	0.020	0.0056	$<10^4$	0.0163	0.0081
4	43.0 ± 0.5	.95	0.109	0.019	0.0055	0.008	0.0151	0.0047
1	42.6 ± 0.5	.95	0.176	0.017	0.0057	0.006	0.0079	0.030
2	42.6 ± 0.5	1.42	0.283	0.023	0.0064	0.015	—	—
7	30.0 ± 0.1	1.42	0.0532	0.0007	0.00095	$<10^5$	0.00286	0.0077
8	30.0 ± 0.1	1.42	0.0519	0.0011	0.00058	$<10^5$	0.00290	0.0119
10	14.5 ± 0.1	1.42	0.0118	0.00074	0.00024	$<10^6$	0.00069	0.0009
9	14.5 ± 0.1	1.42	0.0063	0.00030	0.00010	$<10^6$	0.00045	0.0008

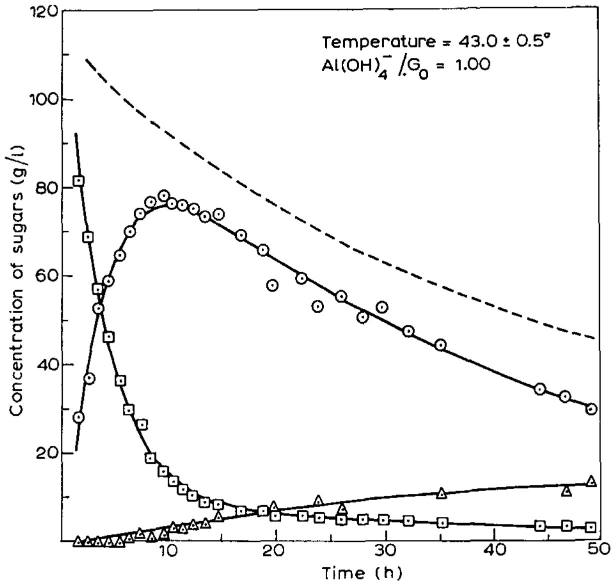

Fig. 1. Typical results from a batch reaction. The points on the graph are experimental data-points, □ for D-glucose, ○ for D-fructose, and △ for D-psicose. The solid lines are the curves computed from the specific rates reported in Table II, run 5. The dashed line represents the sum of the three other solid lines.

The accuracy of the rate constants is subject to the experimental error involved in the data collection and mathematical technique. Tests of the mathematical technique with data generated indicated that the mathematical procedure determined the rate constants accurately. When random error was introduced to the data generated, however, the degree of accuracy of rate constants was diminished according to the magnitude of the rate constants. Random error increased the uncertainty of the smaller specific rate-constants, while only slightly increasing the uncertainty of the specific rate-constants having the greatest magnitudes.

Examination of Table II shows that runs 5 and 6 are duplicate experiments. They give an estimate of the experimental error involved in determining the rate constants. Runs 7 and 8 may also be used as duplicate runs, as the addition of 1% 2-hydroxypyridine had an insignificant effect. Examination of the rate constants shows that k_1 (D-glucose–aluminate to D-fructose–aluminate) is approximately one order of magnitude greater than the other rate constants. This high value of k_1 decreases the relative accuracy of the other rate-constants, but allows a high accuracy in the determination of k_1. It should be noted that rate constants determined from runs 1 and 2 are not so accurate as those from later runs, because of experimental variations; they should be used with greater variance limits than those calculated from duplicate runs.

The rate–temperature data were correlated by using the Arrhenius relationship. Runs 12, 7, 8, and 9 at a molar ratio of 1.42 (aluminate ion : initial D-glucose), and runs 11 and 1 at a molar ratio of 0.95 showed similar activation-energies for k_1, as shown in Fig. 2. The upward shift in the straight line corresponds to increased ratios of aluminate to initial D-glucose, and thus also increased pH of the solution. The number beside each point indicates the run number from which it was obtained.

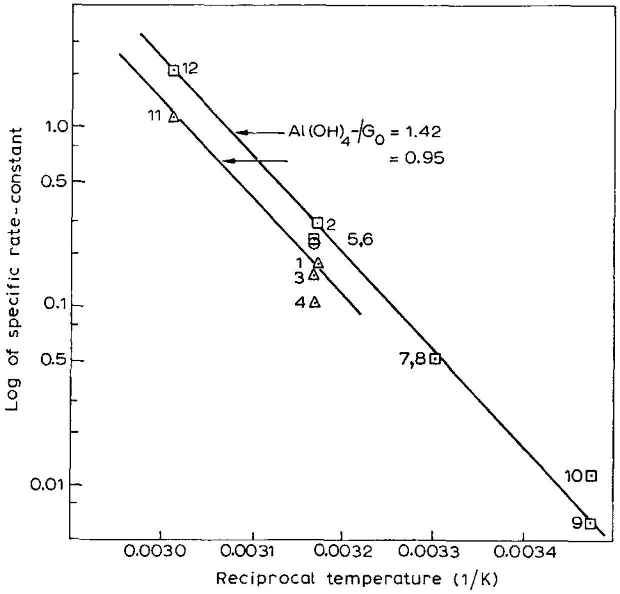

Fig. 2. Arrhenius correlation of the k_1 specific rate-constant at 1.42 $Al(OH)_4^-/G_0$. The number next to each point indicates corresponding run numbers. The slope of the lines indicates that the activation energy of the specific reaction is 24.5 kcal/mol.

Points 3 and 4 in Fig. 2 were conducted with acetic acid added in increased amounts, in order to lower the pH progressively. Point 10 indicates the change in the k_1 rate-constant caused by increasing the pH through addition of sodium hydroxide.

The addition of acetic acid to lower the pH of the reaction appeared to increase the relative rate of degradation of D-fructose–aluminate and D-psicose–aluminate. This may be rationalized by a suspected interaction of acetate ion with the aluminate, and thus interference with the formation of stable D-fructose–aluminate and D-psicose–aluminate complexes. By comparing runs 9 and 10, the addition of sodium hydroxide tends to increase all of the rate constants; however, the increase does not appear to be proportional to the hydroxide ion concentration over the range tested. This factor may be due to interaction of sodium ion with the sugars.

The activation energy of the D-glucose–aluminate to D-fructose–aluminate reaction was found by least-squares, linear regression to be 24.5 kcal/mol. Table III summarizes the Arrhenius plots for a ratio of 1.42 Al(OH)E/G_0 for the other specific rate-constants of the model. The standard errors in the activation energy and frequency factor of the individual constants are also given in Table III. The *F* test, also reported in Table III, is a standard test for significance of correlation; in general, the higher the *F* test value, the better the correlation. No standard error was reported for the (k_4) D-psicose–aluminate degradation-reaction because only two points were used.

TABLE III

SUMMARY OF ACTIVATION CONSTANTS[a] AT 1.42 RATIO, $Al(OH)_4^-/G_0$

Specific rate-constant	*Activation energy (E) kcal/mol* ± *standard error*	*Frequency factor ln* k_0 ± *standard error*	F *Test*
G → F k_1	24.53 ± 0.28	37.8 ± 0.5	7695.1
F → G k_2	29.02 ± 6.1	41.8 ± 10.0	22.9
F → P k_3	27.47 ± 2.13	38.6 ± 3.5	166.3
P → D k_4	25.5	36.2	—
F → D k_5	26.13 ± 1.82	37.8 ± 3.0	206.5
G → D k_6	25.55 ± 1.45	37.7 ± 2.4	310.4

[a] Determined by the least-squares method using the Arrhenius model $\ln k = \ln k_0 - E/R(1/T)$.

MATHEMATICAL AND EXPERIMENTAL PROCEDURES

Mathematical techniques for determining rate constants. — Using the reaction scheme shown in ref. 1, Fig. 3, differential equations may be written describing the formation and depletion of each species. By assuming a specific pH and temperature, these equations become linear, simultaneous, first-order equations having constant coefficients which, in vector notation, can be written as:

$$\frac{\mathrm{d}w}{\mathrm{d}t} = \mathrm{A}\, w,$$

where

$$\mathrm{A} = \begin{bmatrix} -(k_1 + k_6) & k_2 & 0 \\ k_1 & -(k_2 + k_3 + k_5) & 0 \\ 0 & k_3 & -k_4 \end{bmatrix},$$

and

$$w = \begin{bmatrix} \mathrm{G} \\ \mathrm{F} \\ \mathrm{P} \end{bmatrix}$$

A solution for this equation[3] can be written as:

$$w = \sum_j c_j\, z_j \exp(\lambda_j t), \quad \text{where } \lambda_j = \text{eigen value of A, and}$$
$$z_j = \text{eigen vector corresponding to } \lambda_j.$$

With initial-value data, the constants c_j can be calculated.

The calculated changes in concentration of the species were then compared with the experimental data, collected at constant temperature, by minimizing the squared differences between the two. The solution procedure was as follows:

1. Make an initial guess as to the rate constants, the A matrix.
2. Calculate the eigen values, λ_j, and eigen vectors, z_j.
3. Compute the c_j constants from initial conditions.
4. Compare the computer-generated data with the experimental data by summing the squared differences.
5. Use an optimization routine to minimize the sum of the squares by repeating steps 1–4.

Batch reactor procedure. — A water bath equipped with a Haak controller-circulator was set to a desired temperature. A 250-ml vacuum flask was positioned with a magnetic stirrer and apparatus to maintain an oxygen-free atmosphere. Sodium aluminate solution[1] was then added to the flask and allowed to come to bath temperature. Dry sugar was added with constant mixing, and this operation was recorded as time zero. The temperature and pH of the reaction were monitored, and at regular time-intervals the mixture was sampled by withdrawing 1-ml aliquots by means of a glass pipet. The samples were immediately quenched by adding an appropriate amount of phosphoric acid solution (2–5 ml) to bring the pH to 6.8–7.0. The samples were centrifuged, and the decanted liquid saved for later analysis by sealing with parafilm and storing at 3°. The samples were analyzed by the same methods presented in ref. 1.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

Lower reaction-temperatures favor higher peak yields of D-fructose–aluminate, because of the low activation-energy of the k_1 rate-constant relative to the reverse reaction and degradation reactions. Projected reaction-data indicate that a yield of 60% D-fructose with total degradation products of 3.6% may be obtained by a batch reaction operated at 0°. D-Psicose–aluminate is a major product of this reaction, but its concentration is also minimized by lower reaction-temperatures. The degradation products of the sugar–aluminate isomerization should be characterized, as this may lead to specific products of possible commercial volume and value. The effect of pH on the reaction should be studied in more detail, with the possibility of selective product-distribution control. Various methods could be tested in order to lower the pH without interfering with the sugar–aluminate complexes.

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