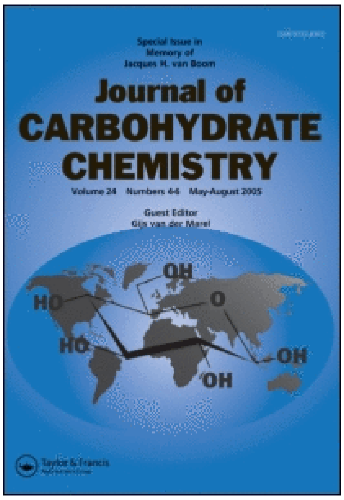

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HYDROTHERMAL DEGRADATION AND KINETIC STUDIES OF 1,3-DIHYDROXY-2-PROPANONE AND 2,3-DIHYDROXYPROPANAL

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ABSTRACT

The equilibrium of 1,3-dihydroxy-2-propanone (dihydroxyacetone) and 2,3-dihydroxypropanal (glyceraldehyde) and their dehydration reaction to methylglyoxal has been studied in the range of 180 - 240 °C under hydrothermal reaction conditions. A reaction mechanism for the conversion of these C-3 compounds was formulated which allowed the calculation of the product yields. In the investigated temperature range both compounds produce a maximum of 30-40% of methylglyoxal.

INTRODUCTION

As the production of energy carriers and chemical raw materials from biomass matter, e.g. straw and wood, is gaining in importance, the investigation of biomass degradation products attracts increasing interest as well.[1-3] In addition to acid hydrolysis[4,5] and alkali hydrolysis[6] newer processes such as enzymatic hydrolysis[7] and hydrothermolysis[8-10] are on the threshold of technical application for the utilization of

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biomass. In the hydrothermal process, ligno-cellulosic biomass is decomposed into low-molecular components by means only of water at elevated temperature and pressure. At temperatures of 180-200 °C hemicellulose and soluble lignin components are dissolved, at 280 °C the cellulose part is degraded into monomeric carbohydrates such as glucose, and at over 300 °C the residual lignin can be transformed into soluble compounds.

In prior studies[11,12] it was found that the monosaccharides formed under hydrothermal reaction conditions at 280 °C are further converted (unless they are quickly eluted from the reaction vessel) mainly by two reaction mechanisms: the formation of heterocyclic by-products, such as furfural and hydroxymethylfurfural, through elimination of water; and the cleavage of hexoses (e.g. glucose) into C-3 compounds, e.g. dihydroxyacetone (I) and glyceraldehyde (II). Also, the combination of both reactions can occur. These C-3 degradation products are also obtained as by-products in alkaline and acid hydrolyses of carbohydrates.[13] The product formation and the isomeric equilibrium of (I) and (II) under hydrothermal conditions are of special interest for our process and were therefore investigated at temperatures of 180 - 240 °C in this work. At the same time the kinetic studies should show to which maximum amounts of methylglyoxal (III) hydrothermal treatment can lead.

RESULTS AND DISCUSSION

Figs. 1-4 show the degradation experiments of (I) and (II) under the same reaction conditions but different degradation temperature. In the investigated temperature range the decrease in concentration of (I) and (II) is a first order reaction. If (I) is used as the initial substance, (II) and (III) occur in their maximum yields at approx. 1% and 30-40% of the (II) respectively. When hydrothermolyzing (II), on the other hand, (I) and (III) are

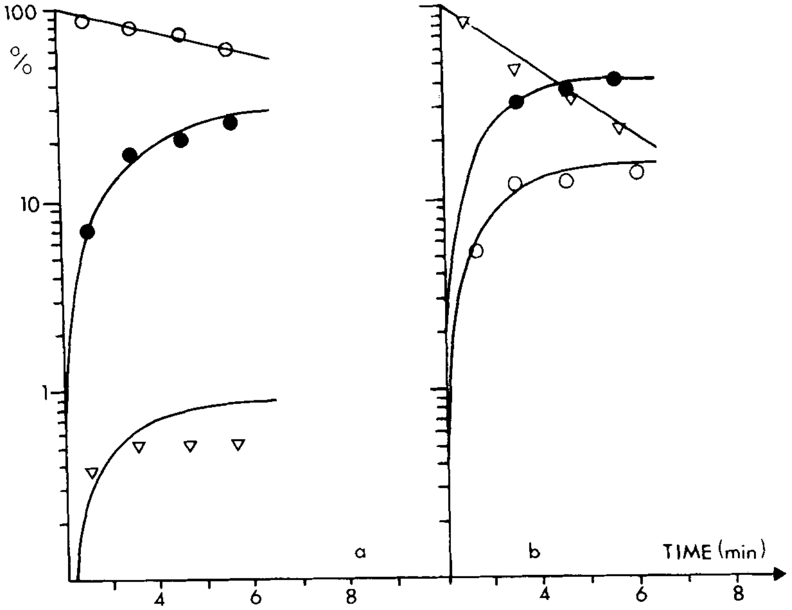

FIG. 1. Hydrothermolysis of a) dihydroxyacetone (I) and b) glyceraldehyde (II) at 180 °C.
o (I), ▽ (II), ● (III)
Plotted curves were calculated.

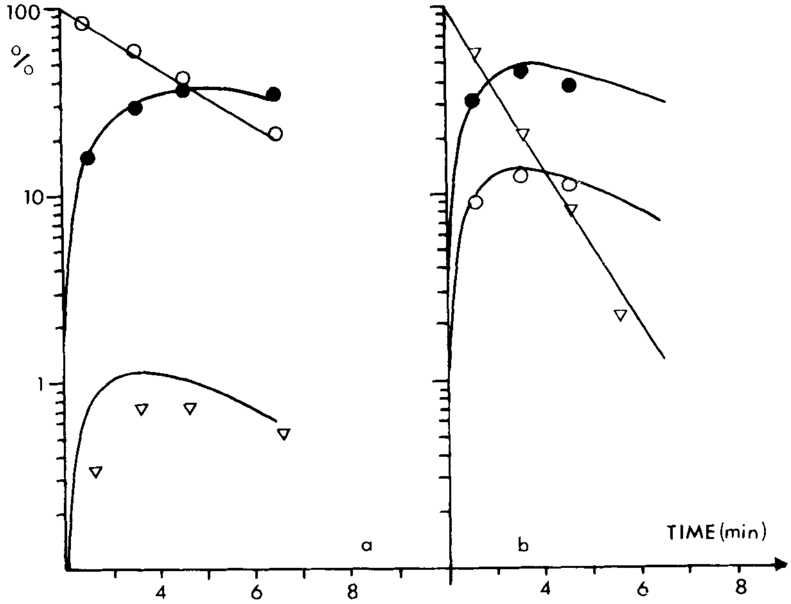

FIG. 2. Hydrothermolysis of a) dihydroxyacetone (I) and b) glyceraldehyde (II) at 200 °C.
o (I), ▽ (II), ● (III)
Plotted curves were calculated.

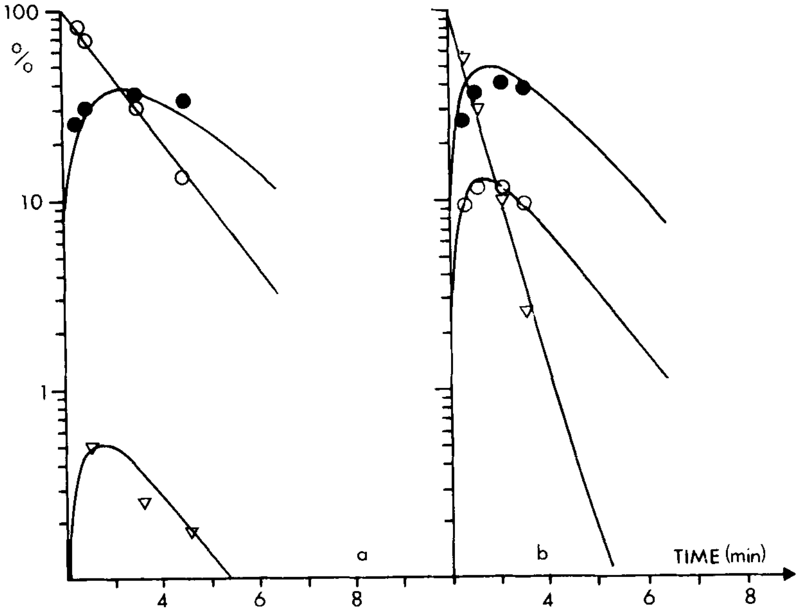

FIG. 3. Hydrothermolysis of a) dihydroxyacetone (I) and b) glyceraldehyde (II) at 220 °C.
o (I), ∇ (II), ● (III)
Plotted curves were calculated.

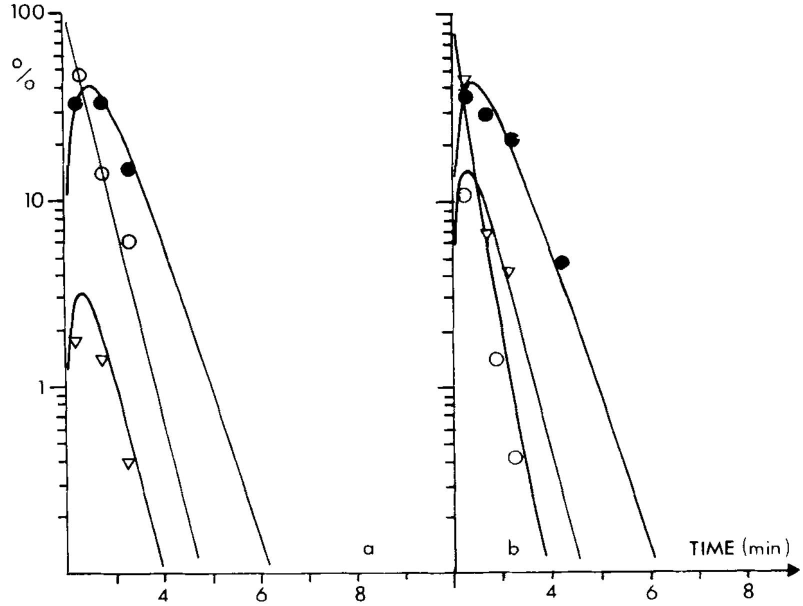

FIG. 4. Hydrothermolysis of a) dihydroxyacetone (I) and b) glyceraldehyde (II) at 240 °C.
o (I), ∇ (II), ● (III)
Plotted curves were calculated.

found in amounts up to 12% and 40% of the (II) respectively. A reverse reaction of (III) to (II) and (I) was not found. Hexoses could not be determind (detection limit:0.1 mg/mL). Therefore a recombination of the C-3 compounds into hexoses does not occur. Under hydrothermal conditions (III) is converted into lactic acid only at relatively high temperatures (>220 °C).

Fig. 5a shows the generally accepted reaction mechanism for the interconversion of the C-3 compounds with an enediol as intermediate state. Under acidic conditions and low temperatures (I) is dehydrated to (III) faster than (II).[13] The mathematical treatment of our experiments according to this scheme did not, however, give satisfactory results. The hydrothermal degradation differs characteristically from acidic degradation experiments. In the former case (III) is formed more rapidly from (II) than from (I). A slightly different scheme for (I) and (II) interconversion is therefore proposed in Fig. 5b.

According to Fig. 5b the following reaction equations are formulated:

$$\frac{d[I]}{dt} = - k_1 \cdot [I] - k_3 \cdot [I] + k_2 \cdot [II] \qquad (1)$$

$$\frac{d[II]}{dt} = - k_2 \cdot [II] - k_4 \cdot [II] + k_1 \cdot [I] \qquad (2)$$

$$\frac{d[III]}{dt} = - k_3 \cdot [I] + k_4 \cdot [II] - k_5 \cdot [III] \qquad (3)$$

The equation system for these first order reactions is solved exactly and can be found in ref 14. The best fits for these equations are given as plotted curves with the experimental points in Figs. 1 to 4. Table 1 summarizes the rate constants (k) so obtained for the different reaction temperatures. The calculated curves agree well with the experimental points so that the introduced kinetic model, which neglects the enediol for-

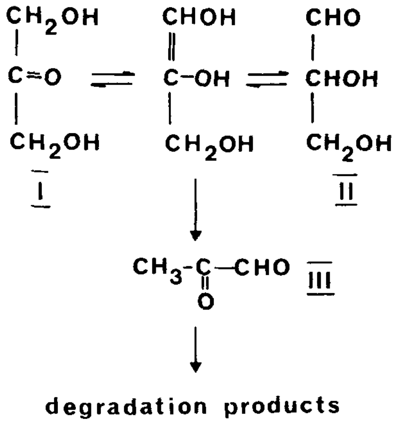

FIG. 5a

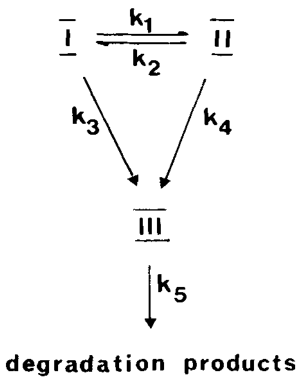

FIG. 5b

FIG. 5a. Reaction mechanism of the hydrothermal degradation of (I) and (II) with an enediol as intermediate state.

FIG. 5b Simplified reaction mechanism for the kinetic treatment of the hydrothermal degradation of (I) and (II) in the range 180-240 °C.

TABLE 1

Calculated Rate Constants for various Reaction Temperatures based on Data of FIG. 5b.

°C	180	200	220	240	E[kJ/mol]	A $[s^{-1}]$
$[min^{-1}]$						
k_1	0.003	0.01	0.01	0.15	130.5	$5.6 \cdot 10^{10}$
k_2	0.052	0.12	0.24	0.70	81.2	$2.0 \cdot 10^{6}$
k_3	0.065	0.17	0.38	1.20	91.5	$3.8 \cdot 10^{7}$
k_4	0.145	0.38	0.83	1.50	75.2	$1.1 \cdot 10^{6}$
k_5	0.090	0.18	0.38	1.00	76.9	$1.1 \cdot 10^{6}$

mation, can be accepted as a good interpretation of the experiments. In Fig. 6 the calculated rate constants (k_1 to k_5) are plotted logarithmically against the inverse absolute temperature.

The main influence on the (I) consumption is due to the k_1 and k_3 reaction constants. From Figs. 1a to 4a it can be seen that the reverse reaction k_2 can be neglected because (II) rise to only very low concentrations. Although k_1 adds only a small contribution to the overall reaction, equation (1) can be written:

$$\frac{d[I]}{dt} \approx -(k_1+k_3)\,[I] \qquad (4)$$

In a similar way the disintegration reaction of (II) is mainly influenced by the constants k_2 and k_4. The rate constant k_1 is so low that equation 2 can be modified to:

$$\frac{d[II]}{dt} \approx -(k_2+k_4)\,[II] \qquad (5)$$

The measured and calculated rate constants (k_1+k_3) and (k_2+k_4) are given in Table 2. Very good agreement between the experimental and computer data is obtained. Straight lines representing these values are also plotted in Fig. 6. The subordinate influence of k_1 and k_2 can easily be seen. Another interesting result is that (k_1+k_3) approaches (k_2+k_4) at increasing temperatures. In a high temperature region the first reaction constants expression can therefore exceed the second, as is found with acidic treatment.[13]

The activation energies of k_2,k_3,k_4 and k_5 lie in the narrow range between 75.2 and 91.5 KJ/mol (Table 1). Only the activation energy of k_1 is considerably higher, but due to the low k_1-values and relatively high errors this result has only limited significance.

The frequency factor values (A) are between $1.1\cdot10^6$ and $3.8\cdot10^7$ (s^{-1}), with the exception of that for k_1 which again is considerably higher (Table 1).

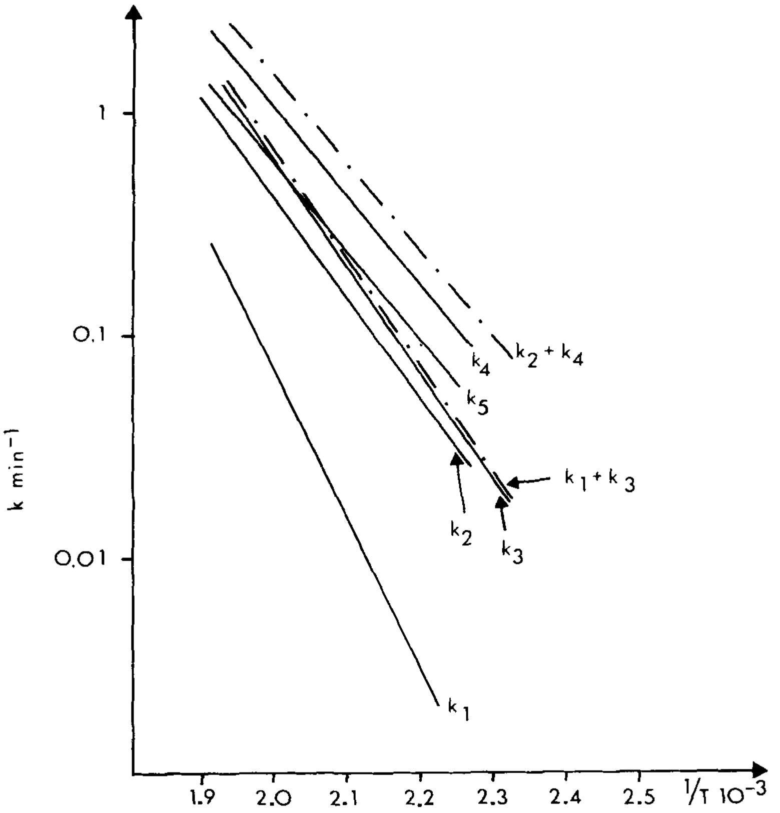

FIG. 6 Arrhenius plot of the calculated (---) and measured (-- --) rate constants

The results of the 240 °C experiment (Fig. 4) show that after 3 minutes reaction time the initial (I) and (II) compounds are consumed up to a remainder of 2 and 0.3% respectively. This explains why in an earlier work (ref. 12), using D-(U-14C) glucose and D-(U-14C) fructose, (II) could not be determined. Under these temperature conditions the degradation of the (II) formed is so fast that the concentration (and specific radioactivity) fell below the detection limit. Methylglyoxal (III) is the main reaction product in the scheme (Fig. 5b) discussed. The maximum yields are approx. 40% of the initial (I) or (II). In the hydrothermal treatment of many carbohydrats the latter two occur as reaction products. Hydrothermolysis is therefore a possible pro-

TABLE 2

Comparison of Measured and Calculated Rate Constants of (I) and (II) Disintegration.

	(I) (k_1+k_3)		(II) (k_2+k_4)	
T°C	measured	calculated	measured	calculated
	$[min^{-1}]$	$[min^{-1}]$	$[min^{-1}]$	$[min^{-1}]$
180	0.068	0.065	0.201	0.197
200	0.173	0.180	0.499	0.500
220	0.384	0.390	1.073	1.070
240	1.263	1.350	1.982	2.200

duction process for (III), a compound which has considerable potential use in organic synthesis (e.g. preparation of vitamin A).

EXPERIMENTAL

Materials.

(I) and (II) used were of analytical grade purchased from Fluka, Buchs, Switzerland. Solutions of 10 mg (I) and (II) per 100 mL of water (distilled, degassed) were prepared.

Kinetic and hydrothermal measurements.

The triose solutions (4 mL) were put into stainless steel autoclaves (180x8 mm I.D.) and kept in an oil bath at 180-240 °C for a predetermined period of time. The heating-up period, which was deducted from the total reaction time, was determined using a thermocouple placed inside the autoclave and was found to be 90 s at 240 °C. The reaction was stopped in an ice-water mixture. Some kinetic experiments were carried out in duplicate and the deviations were less than 4%.

Analytical methods.

(I), (II) and degradation products were analyzed using HPLC. The samples were determined directly without pretreatment using a HPX 87 H column.[15,16]

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