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Note

Four-carbon model compounds for the reactions of sugars in water at high temperature*

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As early as 1932, Hurd and Isenhour[2] employed the results of experiments involving glycerol, 1,4-butanediol, and 1,2,4-butanetriol to gain insight into the mechanism of furfural formation from pentoses. They detected no products from glycerol after refluxing for 2 h in 3.9 N aq. HCl, thereby demonstrating the acid-catalyzed dehydration mechanism to be very slow at temperatures near 100°. On the other hand, after heating a solution of 1,4-butandiol in sulfuric acid for 2 h at 65–70°, the same authors obtained a 76% yield of tetrahydrofuran. Similarly, they noted that 1,2,4-butanetriol may be converted into 3-hydroxytetrahydrofuran on boiling with water. Since that time there have been extensive studies of anhydride formation from alditols[3,4], however all such studies have generally utilized strong acids and high temperatures. These results clearly establish and alerted us to the potential role of acid-catalyzed, intramolecular nucleophilic substitution (etherification) mechanisms in the dehydration of aldoses and ketoses. In subsequent papers we shall elaborate upon the involvement of such reactions in the formation of furfural and 5-(hydroxymethyl)-2-furaldehyde (HMF) from aldoses.

Recently Ramayya *et al.*[5] reported experimental investigations of the acid-catalyzed dehydration of ethanol, 1-propanol, and glycerol in liquid water at 34.5 MPa and temperatures ranging from 320° to 400°. After 20 s, in the presence of 1–30 mM sulfuric acid, essentially 100% relative molar yields of ethylene were obtained from 0.5M (or less) ethanol. Similar results were obtained from 1-propanol. Clearly, the high temperatures involved in these experiments facilitated the acid-catalyzed elimination reaction, leading to the selective dehydration of the alcohol. When the concentration of the alcohol reactant exceeded M, the appropriate ether was detected in the reaction products. Thus,

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*Part 2 of the series Kinetic studies of the reactions of ketoses and aldoses in water at high temperature. For part 1, see ref. 1.

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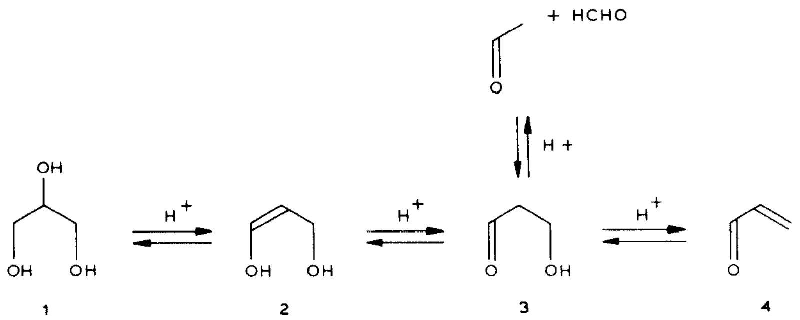


Scheme 1

acid-catalyzed etherification reactions can also be important in liquid water at these high temperatures. Under similar conditions, glycerol (**1**) reacted to form acrolein, acetaldehyde, and formaldehyde. The stepwise mechanism [5] of acrolein formation (see Scheme 1) involved (*i*) the acid catalyzed E2 (or possibly E1) elimination of the 2-hydroxyl group, forming the enol **2**, (*ii*) a de-enolization to the aldehyde **3**, and (*iii*) a final acid-catalyzed dehydration leading to product acrolein (**4**). It should be noted that the conversion of **1** to **3** is a pinacol rearrangement. Formaldehyde and acetaldehyde were products of a reverse aldol reaction involving intermediate **3** as the reactant. In the absence of acid, the three alcohols were stable in the temperature range 300–400°. Thus, at high temperatures, trace amounts of acid are able to catalyze a wide variety of dehydration reactions involving E2/E1 eliminations and related SN2 (or possibly SN1) substitutions, accompanied by rapid pinacol rearrangements and reverse aldol reactions.

Unfortunately, with respect to a contribution to our understanding of the reactions of reducing sugars, these earlier experiments[5] employed somewhat higher temperatures than those which offer optimal yields of furfural from xylose and HMF from glucose and fructose. In this paper, therefore, we report studies of the aqueous-phase reaction chemistry of glycerol, 2-propanol, 1,4-butandiol, tetrahydrofuran, glyceraldehyde, pyruvaldehyde, and dihydroxyacetone in the presence and absence of H_2SO_4 at 250°. These model compounds were selected to illustrate the relative rates of acid-catalyzed E2/E1 dehydrations, acid catalyzed inter- and intra-molecular SN2/SN1 etherifications, base-catalyzed β-eliminations, benzilic acid rearrangements, and acid/-base-catalyzed enolizations–isomerizations at 250° in liquid water. All of these reactions could play an important role in the high-temperature formation of furaldehydes from pentoses and hexoses.

EXPERIMENTAL

Apparatus and experimental procedures.—These were the same as those described in the preceding paper[5]. Reagents were used as received in their purest, commercially

TABLE I

Reactions in Aqueous Sulfuric Acid at 250° and 34.5 MPa

Acid (M)	*Substrate (conc.)*	*Conversion* (%)	*Product(s)*	*product yield*(%)
0.01	Glycerol (0.1M)	1	Acrolein	[a]
0	1,4-Butanediol (0.1M)	0		0
0.01	1,4-Butanediol (0.1M)	20	Tetrahydrofuran	22
0.01	Tetrahydrofuran (0.1M)	12	1,4-Butanediol	12
0.01	Glyceraldehyde (0.05M)	100	Pyruvaldehyde	19
			Lactic acid	40
0.01	Pyruvaldehyde (0.07M)	93	Lactic acid[b]	31
0.001	Dihydroxyacetone (0.1M)	75	Glyceraldehyde	trace
			Pyruvaldehyde	38
			Lactic acid	15

[a] Not detected, [b]Other products include acetic acid and acetol.

available form. Each was shown to be free from significant contamination by either gas chromatography or high performance liquid chromatography.

RESULTS AND DISCUSSION

Table I displays the results of an acid-catalyzed glycerol dehydration experiment at 250°. The residence time (100 s), reactant concentration (0.1M) and H_2SO_4 concentration (0.01M) are representative of values employed in our work on ketoses and aldoses. Only a small conversion of glycerol was observed, and no reverse aldol reaction products (formaldehyde and acetaldehyde) were detected. Acrolein was detected by g.l.c.–m.s., but not by l.c.. Evidently the rate of the acid-catalyzed E2/E1 dehydration for this triol is very low at 250°, and the rate of the reverse aldol (fragmentation) reaction is negligible.

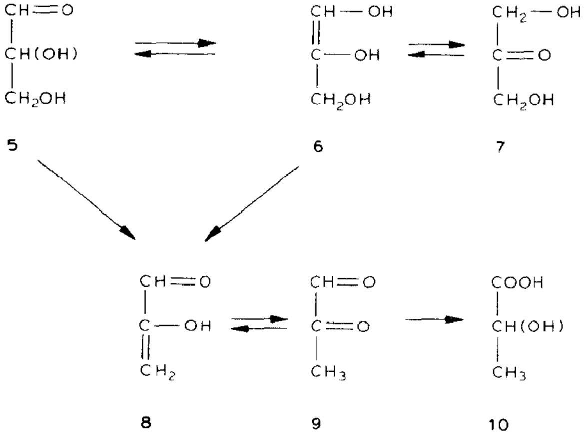
Qualitative analysis by g.l.c.–m.s. of a similar experiment, involving a higher concentration (2M) of reactant 2-propanol and 0.01M H_2SO_4, revealed the formation of only two major products: propene and diisopropyl ether. Quantitative analysis was not completed because of difficulties in analyzing the ether, which was present in both the liquid and vapor phases. However, the mere observation of ether formation from a dilute ($\sim$4% by mole) mixture of alcohol and acid in water calls attention to the need for careful scrutiny of the potential role of intramolecular SN2/SN1 etherification reactions in the dehydration of aldoses and ketoses to furaldehydes.

Table I also sheds some light on the importance of intramolecular etherification reactions by presenting results of experiments involving 1,4-butanediol and tetrahydrofuran (THF). Without acid the butanediol is stable in water at 250°, but the presence of 0.01M H_2SO_4 catalyzes a 20% conversion of the diol into THF after 100 s.

Conversely, 0.01 M H_2SO_4 catalyzes a 12% conversion of THF into butanediol after 100 s at 250°. Clearly equilibrium between the two species was not reached after 100 s. An experiment involving 0.05M fructose as catalyst (no acid) also resulted in the formation of some THF (detected by g.l.c.–m.s.). Apparently fructose, or more likely some reaction product thereof, is sufficiently acidic to catalyze the etherification reaction. These results clearly indicate the probable role of intramolecular, acid catalyzed SN2/SN1 etherification reactions in the formation of furaldehydes from aldoses and ketoses.

Glyceraldehyde and dihydroxyacetone are major reverse-aldol reaction products of hexoses in water at elevated temperatures (see preceding paper[1]). To investigate the subsequent reaction chemistry of these species in water, several experiments were executed. Table I shows that, in the presence of 0.01 M H_2SO_4, glyceraldehyde completely disappears after 100 s at 250°. The major products are pyruvaldehyde and lactic acid. Presumably glyceraldehyde first loses water to form pyruvaldehyde, which subsequently undergoes a benzilic acid rearrangement to form lactic acid. Table I corroborates this presumption by showing lactic acid to be the major product obtained from pyruvaldehyde under these conditions. In the preceding paper we noted that the benzilic acid rearrangement occurs in acid as well as in alkali, and concluded that even after addition of acid, water (as a Brønsted base) remains an effective catalyst for the rearrangement reaction. Hence, pyruvaldehyde is detected in acid-catalyzed degradation of glyceraldehyde, but still reacts to form lactic acid at a significant rate. Many minor products were detected in both experiments involving glyceraldehyde and pyruvaldehyde as reactants, but were not quantified. We believe these minor products account for our deficient carbon balance in these experiments.

After 33 s in the presence of mM H_2SO_4 two major products result from reactions involving the three-carbon ketose dihydroxyacetone: pyruvaldehyde and lactic acid (see Table I and Scheme 2). A trace of glyceraldehyde was also detected by l.c.. If glycer-



Scheme 2

aldehyde (**5**) is intermediate in the formation of pyruvaldehyde (**9**) and lactic acid (**10**) from dihydroxyacetone (**7**), then the rate of isomerization (enediol formation) must be low relative to the subsequent dehydration reaction (see Scheme 2). We note that dehydration to the enol **8** of pyruvaldehyde may occur either from glyceraldehyde (**5**) or its enol **6**, but at present the evidence available under these experimental conditions is inadequate to decide between the two possibilities. The significant presence of pyruvaldehyde (**9**) relative to lactic acid (**10**) reveals the rate of the benzilic acid rearrangement to be of the same order of magnitude as the dehydration reaction. Again we note that water as a Brønsted base catalyzes the benzilic acid rearrangement of pyruvaldehyde to lactic acid, even in the presence of 0.001 M H_2SO_4. In a closely related work, Bonn *et al.*[6] reported temperature-dependent rate constants for the disappearance of dihydroxyacetone in water without acid. If the value for this rate constant is extrapolated from their reported value at 240° to 250°, a 47% conversion of dihydroxyacetone is predicted. This is somewhat less than the observed conversion (75%) in the presence of acid[6].

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