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KINETICS AND MECHANISM OF THE ACID-CATALYZED REACTIONS OF METHYLATED TRIOSES

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ABSTRACT

In aqueous hydrochloric acid, 2,3-di-*O*-methyl-D-glyceraldehyde and 1,3-dimethoxy-2-propanone undergo acid-catalyzed reactions producing 2-oxopropanal. The kinetics of these two reactions were studied polarographically. The kinetic data obtained and the incorporation of deuterium from the medium into the 2-oxopropanal formed (isolated as 2-methylquinoxaline and analyzed mass spectrometrically), allowed formulation of a mechanism for the acid-catalyzed reaction of both methylated trioses. The mechanisms proposed are in agreement with quantum-chemical calculations of the charge distribution in the compounds studied and in some of their important intermediates.

INTRODUCTION

While the isomerization and epimerization equilibria of monosaccharides and their derivatives have been, in principle, elucidated in alkaline media, the existence of these equilibria in aqueous solutions of mineral acids remains a subject for discussion. It is necessary to distinguish acid-catalyzed reactions of monosaccharides from those occurring in acid medium but which can be catalyzed by bases in the solution[1]. It has, however, been demonstrated that small amounts of D-fructose are formed from D-glucose[2,3] in aqueous solutions of mineral acids, and *vice versa*[4]. The work of Feather *et al.*, using isotope techniques[5–11], has helped to clarify the mechanisms of the acid-catalyzed reactions of monosaccharides.

Studies of the acid–base-catalyzed transformations of monosaccharides and of their methylated derivatives[1] has provided important and interlocking information on the chemistry of sugars. It is known that the position of substitution has a great effect on the character of changes in methylated saccharides brought about by acids or bases. For example, the action of bases on permethylated monosaccharides ends with formation of the enol form of a 3-deoxyaldose, which rapidly undergoes further changes in acid media[1,12]. Not only substitution of monosaccharides at C-2, but also at other positions, may have a marked affect on the reaction course. Thus, the action of mineral acids on methylated pentoses[13] and hexoses[14] produces 2-furaldehyde or its derivatives just as with unsubstituted pentoses and hexoses, except when there is no

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free hydroxyl group at C-5. Substitution of O-5 by a methyl group leads to formation of furanones[15,16].

To obtain convincing data on this type of reaction, it is necessary to study its course quantitatively on simple compounds. In previous work[17], we studied the kinetics on the acid–base-catalyzed reactions of trioses. It was found that the dehydration of trioses is generally acid–base-catalyzed, whereas aldose–ketose isomerization is generally subject only to basic catalysis. It has recently been stated that acid-catalyzed isomerization of trioses can occur to a very small degree[18]. To further clarify the observed changes of monosaccharides and their derivatives, we recently studied the kinetics and mechanism of acid–base-catalyzed enolization of glycolaldehyde and also the acid-catalyzed enolization and hydrolysis its methyl ether[19].

In connection with our previous work[17,19], we studied the kinetics and mechanism of acid-catalyzed reactions of 2,3-di-*O*-methyl-D-glyceraldehyde and 1,3-dimethoxy-2-propanone, to obtain additional information necessary for clarification and generalization of possible mechanisms of these acid-catalyzed changes of monosaccharides and their derivatives.

EXPERIMENTAL

Instruments and apparatus. — The kinetics of the formation of 2-oxopropanal from 2,3-di-*O*-methyl-D-glyceraldehyde and 1,3-dimethoxy-2-propanone was studied in aqueous hydrochloric acid at defined temperature with a precision of $\pm 0.1°$. The reactions were monitored polarographically (Polarimeter type PO4g, Copenhagen). By condensation with *o*-phenylenediamine, the reaction products were converted into the corresponding quinoxaline derivatives, which were analyzed by mass spectrometry on a JEOL JMS-D 100 instrument. Mass spectra were obtained at 70 eV and an emission of 300 μA by using a JGC-20 K gas chromatograph equipped with a 2-m column packed with 3% of OV-225 on Chromosorb WAW DNCS (80–100 mesh). Gas chromatography was performed with a temperature program of 130–270° (6°/min), and an injection-port temperature of 150° Helium (inlet pressure 101.3 kPa) was used as the carrier gas.

Chemicals. — The 2,3-di-*O*-methyl-D-glyceraldehyde required was prepared from D-mannitol by the method of Baer and Fischer[20]: partial hydrolysis of 1,2:3,4.5,6-tri-*O*-isopropylidene-D-mannitol was effected by the method of Horváth and Varga[21], and the 3,4-*O*-isopropylidene-D-mannitol obtained was methylated to 3,4-*O*-isopropylidene-1,2,5,6-tetra-*O*-methyl-D-mannitol according to the method of Kováč[22]. Hydrolysis of this compound in 0.05M sulfuric acid for 3 h at 90° yielded 1,2,5,6-tetra-*O*-methyl-D-mannitol which was purified chromatographically on a column of silica gel with 3:1 benzene–acetone. Pure 1,2,5,6-tetra-*O*-methyl-D-mannitol having b.p. 172°/2.4 kPa, $[\alpha]_D^{20}$ −18° (*c* 1, water) was oxidized to 2,3-di-*O*-methyl-D-glyceraldehyde with aqueous sodium periodate. Sodium periodate (15 g) in water (50 mL) was added in a slow stream with constant stirring to 50 mL of an aqueous solution containing 10 g of 1,2,5,6-tetra-*O*-methyl-D-mannitol; the tempera-

ture of the mixture was maintained between 20–25°. After the oxidant had been added the mixture was kept for ~1 h. The product was then extracted into chloroform and the extract thoroughly dried (potassium sulfate). Distillation under diminished pressure yielded 74% of a clear, colorless, and mobile liquid having b.p. 42°/1 kPa, $[\alpha]_D^{20}$ +92.7° (*c* 1, benzene) and $[\alpha]_D^{20}$ +12.5° (*c* 1, water).

1,3-Dimethoxy-2-propanone was prepared from glycerol through 1,3-dibromo-2-propanol[23] and 1,3-dimethoxy-2-propanol[24], which, after oxidation with potassium dichromate by the method of Brown and Garg[25], yielded the required 1,3-dimethoxy-2-propanone having b.p. 63.5°/2.26 kPa; n_D^{18} 1.4208.

Procedures. — The reaction of 10mM 2,3-di-*O*-methyl-D-glyceraldehyde or 1,3-dimethoxy-2-propanone was conducted in 2.5–6.5M aqueous hydrochloric acid at 50°. Similarly, the reactions of the two compounds studied were performed at the given concentrations in 4.5M hydrochloric acid in the temperature range 20–60°. When monitoring the reaction of 2,3-di-*O*-methyl-D-glyceraldehyde, the decrease in its concentration with time, and from reaction of the 2-oxopropanal produced was measured by the polarographic method we developed[26]. At preset time-intervals, a 0.5-mL sample of the solution was removed and added to 6.5 mL of aqueous isobutylamine of concentration such that the pH of the solution obtained was 9–10. A 50mM solution of *o*-phenylenediamine (1 mL) was added to this solution, and the mixture was allowed to react for 10 min at 20°. Isobutylamine buffer (1.5M, pH 10.4, 2 mL) was then added to this sample and it was transferred to a polarographic vessel thermostatted at 20°. After bubbling pure nitrogen through the sample, the polarographic curve was recorded from −0.5V *versus* a saturated mercurous sulfate electrode. With 1,3-dimethoxy-2-propanone (which, in contrast to 2,3-di-*O*-methyl-D-glyceraldehyde, is stable in dilute aqueous solution and even in strongly alkaline media), the procedure was similar, except that an aqueous solution of lithium hydroxide was used to render the solution mildly alkaline and, after formation of 2-methylquinoxaline, the solution obtained was polarographed in 0.1M lithium hydroxide at 20°. The first-order rate-constants for the acid-catalyzed reactions of 2,3-di-*O*-methyl-D-glyceraldehyde and 1,3-dimethoxy-2-propanone were calculated either from the height of the polarographic waves of 2-methylquinoxaline corresponding to the concentration of 2-oxopropanal formed, or from the polarographic waves of the unreacted, initial components.

Formation, isolation and characterization of products. — (*A*). A 10mM solution of 2,3-di-*O*-methyl-D-glyceraldehyde or of 1,3-dimethoxy-2-propanone (20 mL) was allowed to react in 4.5M hydrochloric acid for 5 h at 50°. The sample was then cooled, made neutral with solid potassium hydrogen carbonate, 2 mL of 0.1M *o*-phenylenediamine was added, and the mixture was kept for 30 min at room temperature. The 2-methylquinoxaline formed passed over into the distillate when most of the aqueous solution was distilled off at normal pressure; the distillate was then extracted with ether. The ethereal solution was dried (sodium sulfate) and evaporated, and the 2-methylquinoxaline obtained was subjected to g.l.c.–m.s. analysis[27]. Similar experiments were conducted with DL-glyceraldehyde and with 1,3-dihydroxy-2-propanone.

(*B*). Experiments as in *A* were conducted in DCl and D_2O. The only difference was that the solution was made neutral with solid calcium oxide after the reaction was complete and the 2-methylquinoxaline formed was extracted directly with ether.

Quantum-chemical calculations of the most-stable conformations and electron distribution in the molecules of D-glyceraldehyde, 1,3-dihydroxy-2-propanone, their methylated derivatives, and protonated and enol forms were performed as described previously[19].

RESULTS

*Kinetics of the formation of 2-oxopropanal from 2,3-di-*O*-methyl-*D*-glyceraldehyde and 1,3-dimethoxy-2-propanone in aqueous hydrochloric acid.* — It was demonstrated as described in the experimental part that aqueous solutions of hydrochloric acid convert 2,3-di-*O*-methyl-D-glyceraldehyde or 1,3-dimethoxy-2-propanone into 2-oxopropanal, as was found for trioses alone[17].

The necessary dependences for calculation of the rate constants for the formation of 2-oxopropanal from 2.3-di-*O*-methyl-D-glyceraldehyde, describing the catalytic effect of hydrochloric acid at the concentrations employed at 30°, are depicted in Fig. 1.

It is clear from Fig. 2 that the measured rate-constants increase more rapidly than the molar concentration of hydrochloric acid and, on the other hand, using the Hammett acidity function (h_0), more slowly than would correspond to a linear dependence. This condition is best fulfilled by the dependence of the rate constants on the mean activity of hydrochloric acid ($a_\pm$), as was found for the dehydration of trioses[17] and also for the enolization of glycolaldehyde and its methyl ether[19].

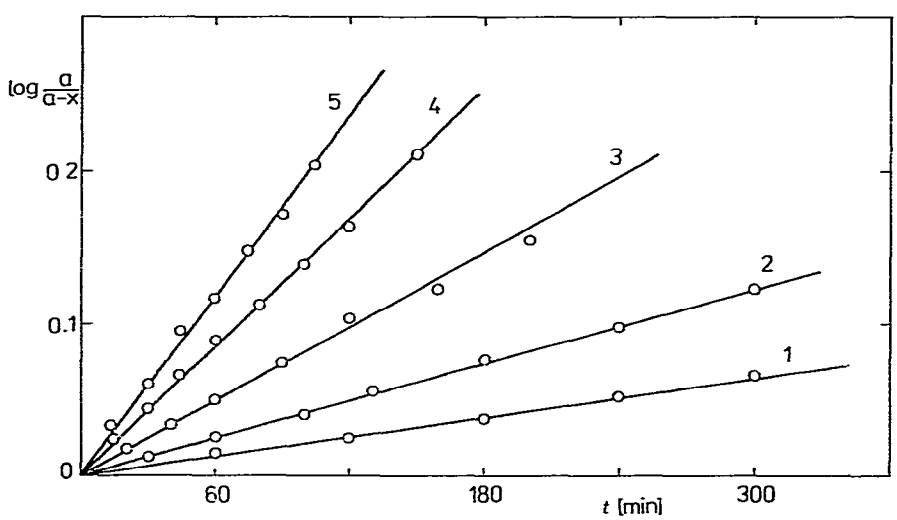


Fig. 1. Kinetic dependence of the formation of 2-oxopropanal from 10mM 2,3-di-*O*-methyl-D-glyceraldehyde studied in 2 5 (1), 3 5 (2), 4.5 (3), 5.5 (4), and 6.0M (5) hydrochloric acid at 50°.

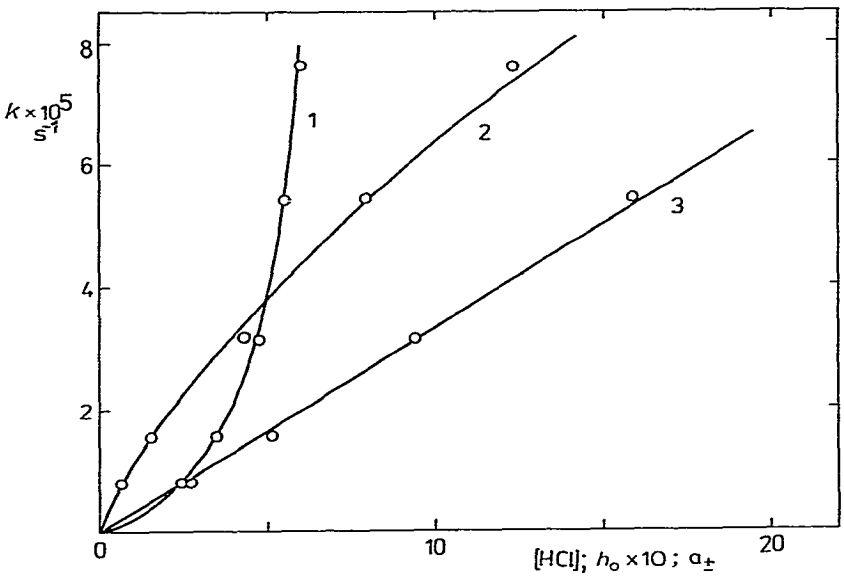


Fig 2. Dependence of the rate constants for the formation of 2-oxopropanal from 2,3-di-*O*-methyl-D-glyceraldehyde on the molar concentration of hydrochloric acid (1), its acidity function (h_0) (2), and mean HCl activity ($a_\pm$) (3), at 50°.

The dependence of the rate constants on the mean activity of hydrochloric acid ($a_\pm$) (Fig. 2, No. 3) yielded a value of $k_{a_\pm} = 0.33 \times 10^{-5}$L.mol^{-1}s^{-1} at 50° for the catalytic constant for the formation of 2-oxopropanal from 2,3-di-*O*-methyl-D-glyceraldehyde.

The reaction of 10mM 2,3-di-*O*-methyl-D-glyceraldehyde forming 2-oxopropanal in 4.5M hydrochloric acid over the temperature range 30–60° was studied to determine the activation energy of the process studied. As in previous work[17,19], the activation energy was found graphically by using the Arrhenius equation, where the appropriate values of the catalytic constants were used in the calculation for the individual temperatures. In this manner, a value of $E_{a_\pm} = 113.6$ kJ.mol^{-1} was found for the activation energy for the catalyzed formation of 2-oxopropanal from 2,3-di-*O*-methyl-D-glyceraldehyde. 1,3-Dimethoxy-2-propanone was treated in aqueous solutions in a manner analogous to that used with 2,3-di-*O*-methyl-D-glyceraldehyde. The dependences of the rate constants measured for the formation of 2-oxopropanal from 1,3-dimethoxy-2-propanone on the molar concentration of hydrochloric acid, the Hammett acidity function (h_0), and the mean activity of hydrochloric acid ($a_\pm$) are depicted in Fig. 3. Here again, the requirements are best fulfilled by the dependence of the rate constants on the mean activity of hydrochloric acid, from which a catalytic-constant value of $k_{a_\pm} = 1.33 \times 10^{-5}$L.mol^{-1}s^{-1} was found for the acid-catalyzed formation of 2-oxopropanal from 1,3-dimethoxy-2-propanone.

A value of $E_{a_\pm} = 86.7$ kJ.mol^{-1} was found for the activation energy for the

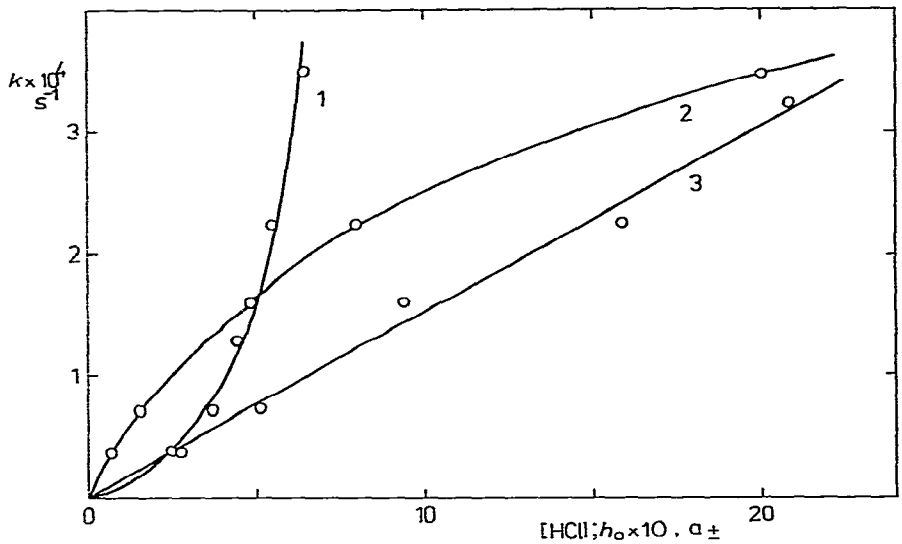


Fig. 3. Dependence of the rate constants for the formation of 2-oxopropanal from 1,3-dimethoxy-2-propanone on the molar concentration of hydrochloric acid (1), the acidity (h_0) (2), and mean HCl activity ($a_\pm$) (3) at 50°.

TABLE I

CATALYTIC CONSTANTS AND ACTIVATION ENERGIES FOR THE ACID-CATALYZED REACTIONS OF GLYCOLALDEHYDE, TRIOSES, AND METHYLATED DERIVATIVES

Compound	$10^5 \times k_{a_\pm}$ *(L.mol^{-1}.s^{-1})*	$E_{a_\pm}$ *(kJ.mol^{-1})*
Glycolaldehyde	1.60	112.2
Methoxyacetaldehyde	0.22	134.6
DL-Glyceraldehyde	0.64	102.5
2,3-Di-*O*-methyl-D-glyceraldehyde	0.33	113 6
1,3-Dihydroxy-2-propanone	1.37	88 8
1,3-Dimethoxy-2-propanone	1.33	86 7

formation of 2-oxopropanal from 1,3-dimethoxy-2-propanone over the temperature range 20–60°.

For clarity, Table I lists the values of the catalytic constants and activation energies for both the acid-catalyzed reactions studied for methylated trioses and also for the free trioses studied earlier[17], as well as for glycolaldehyde and its methyl ether[19].

As has been mentioned, both methylated trioses yield 2-oxopropanal in aqueous solutions of hydrochloric acid, as also demonstrated by the molecular weight and fragmentation of its product with *o*-phenylenediamine, namely, 2-methylquinoxaline[27]. The acid-catalyzed formation of 2-oxopropanal from the two methylated trioses by

using deuterated acid in D_2O and employing mass-spectrometric analysis was shown to yield deuterated 2-methylquinoxaline having molecular weights of 145, 146, and 147. Mass fragmentation of the 2-methylquinoxalines obtained demonstrated that all three deuterium atoms are located in the methyl group, indicating that the incorporation of deuterium occurs only into the methyl group of 2-oxopropanal. The

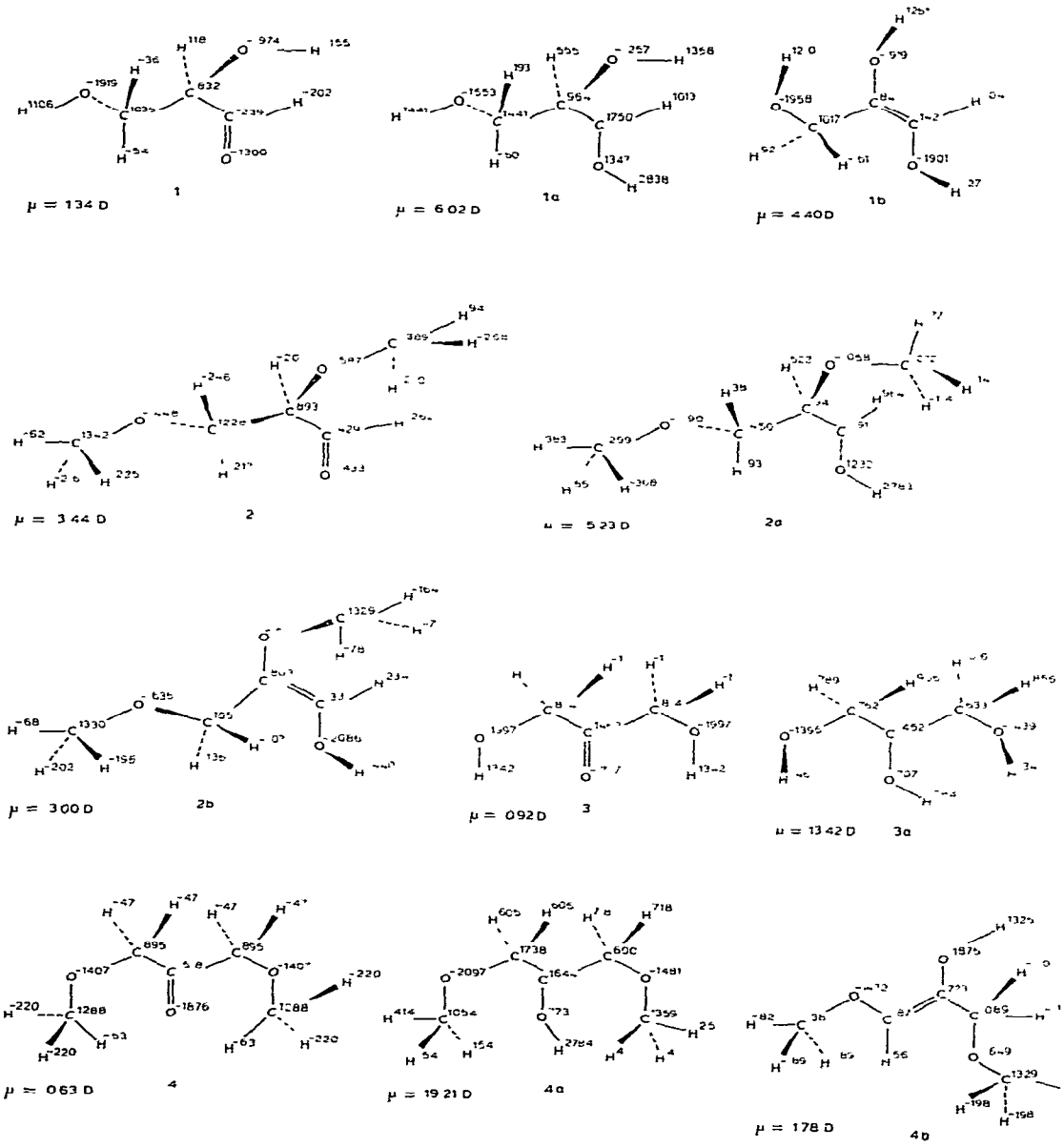


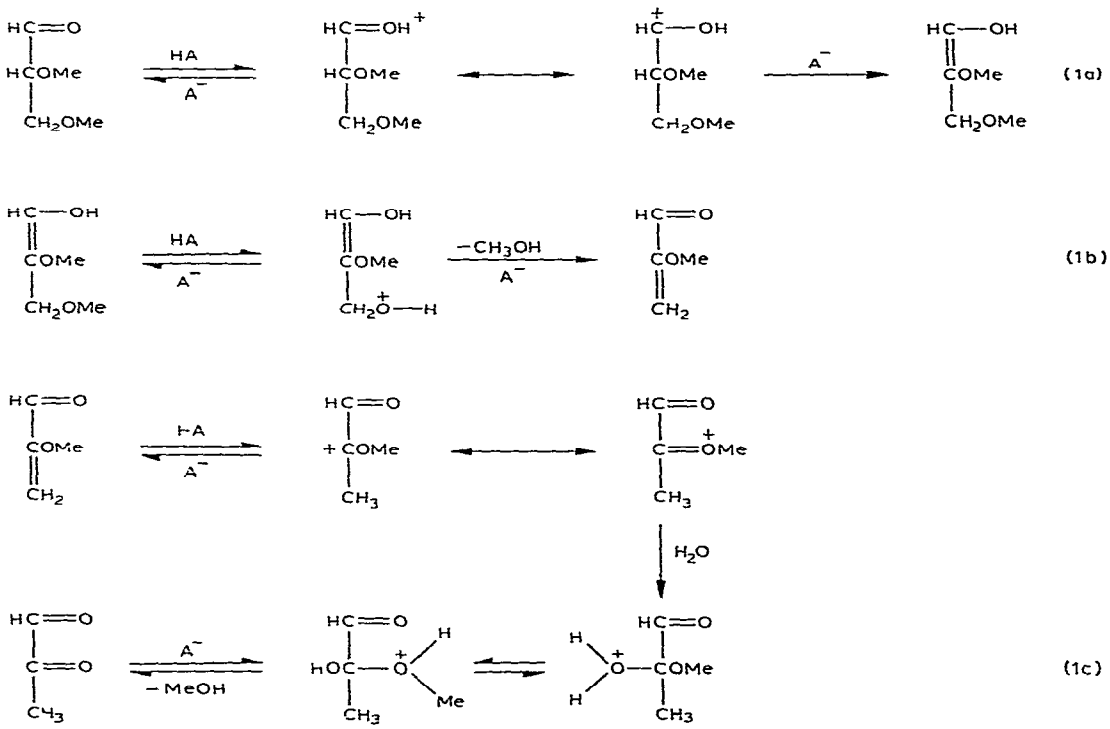
Fig. 4. The charge distribution (in 10^{-4}e) in the most stable conformation of D-glyceraldehyde, 1,3-dihydroxy-2-propanone, and their methylated, protonated, and enol forms.

2-oxopropanal produced from 2,3-di-*O*-methyl-D-glyceraldehyde yielded 2-methylquinoxaline having the following molecular weights and percent composition: 145 (6%), 146 (25%), and 147 (69%). With 1,3-dimethoxy-2-propanone, the methyl group of 2-oxopropanal was also shown to be deuterated to various degrees, as follows from the mass-spectrometric analysis of a mixture of the appropriate 2-methylquinoxalines: 145 (7%), 146 (32%), and 147 (61%).

To obtain further, very important data as a basis for explaining the mechanisms of the acid-catalyzed reactions of the compounds studied, quantum-chemical calculations were performed to find the most stable conformations and electron distribution in the molecules of D-glyceraldehyde, 1,3-dihydroxy-2-propanone, their methylated derivatives, and protonated and enol forms by the method given in a previous report[19]. Fig. 4 schematically depicts the calculated, most-stable conformations of the compounds studied, their most important assumed intermediates, distribution of electronic charges in the given molecules, and their dipole moments. It should be noted that the values of the dipole moments of the protonated forms depend on the choice of coordinate system, which explains the large values for structures **3a** and **4a** (Fig. 4).

DISCUSSION

As with methylated monosaccharides[1,12], the ether group at C-2 exhibits a stabilizing effect on 1,3-dimethoxy-2-propanone against the action of alkalies. This



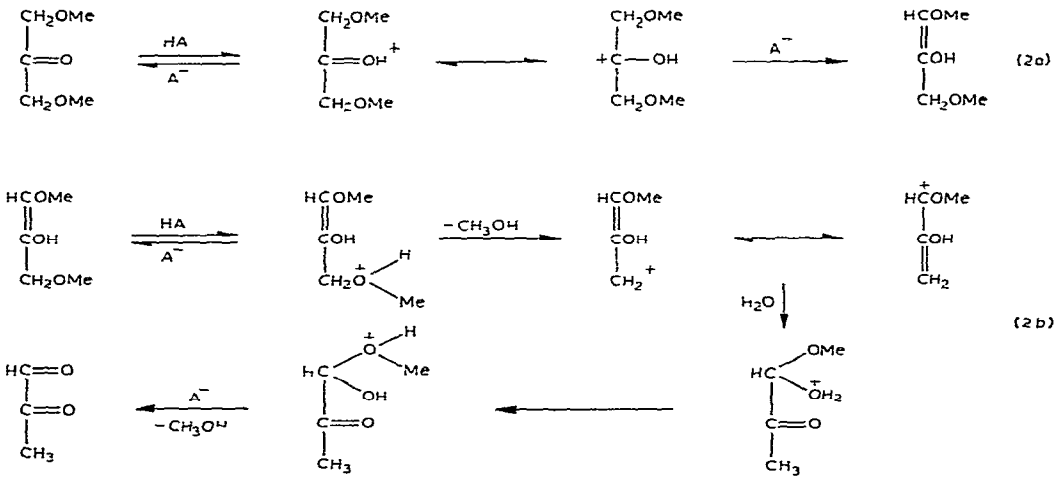
effect was also observed for 2,3-di-*O*-methyl-D-glyceraldehyde, from which methanol is split off in alkaline medium through a β-elimination reaction to yield the relatively stable, 2-methoxypropenal. Consequently, the behavior of methylated trioses in alkaline medium is, in principle, different from that of the free unsubstituted forms, which dehydrate to yield 2-oxopropanal in this medium and in equilibrium mixtures[17]. In contrast, in aqueous mineral acid, both unsubstituted trioses[17] and their methylated derivatives undergo acid-catalyzed reactions with formation of 2-oxopropanal. In both instances, the same product is formed by a different mechanism as a result of the differences in the enol forms of methylated trioses. In agreement with kinetic data for the formation of 2-oxopropanal from 2,3-di-*O*-methyl-D-glyceraldehyde and incorporation of deuterium into the methyl group alone of the final product, the following mechanism is proposed for this acid-catalyzed reaction.

The acid-catalyzed reactions of 2,3-di-*O*-methyl-D-glyceraldehyde consist basically of three independent processes, enolization (*1a*), subsequent β-elimination of methanol (*1b*), and hydrolysis of the 2-methoxypropenal formed, leading to 2-oxopropanal as the final product (*1c*). The enolization of 2,3-di-*O*-methyl-D-glyceraldehyde (*1a*) is generally an acid-catalyzed reaction, similar to that found for glycolaldehyde and its methyl ether[19]. This is a bimolecular type of reaction (A-2 mechanism), in which the slow, and rate-determining, step is the abstraction of a proton by the general base, leading to formation of the corresponding enol form, namely, 2,3-dimethoxy-1-propen-1-ol. This reaction is preceded by a rapidly equilibrating protonation of 2,3-di-*O*-methyl-D-glyceraldehyde with formation of the given mesomeric forms. This acid-catalyzed enolization (*1a*) is the slowest of the three processes, and is the rate-determining step for the whole process. As the following two steps (*1b*, *1c*) are very rapid as compared with the first (*1a*), the rate-constant values obtained characterize the rate of the first, irreversible step A retarding effect of the methoxyl group on the reaction rate as compared with unsubstituted glyceraldehyde[17] and glycolaldehyde[19] was also found here (Table I). The conclusion that no equilibrium system is established in the slow step involving formation of the enol form of 2,3-di-*O*-methyl-D-glyceraldehyde, but that this enol rapidly undergoes subsequent reactions, is confirmed by the fact that deuterium is not incorporated into the aldehyde group of the 2-oxopropanal obtained. These results are also in agreement with those obtained by Feather *et al.*[5], who demonstrated in a series of papers that, in the action of mineral acids on pentoses or hexoses in deuterium oxide or tritium-enriched water, there is no incorporation of these isotopes into the 2-furaldehyde or 5-(hydroxymethyl)-2-furaldehyde produced.

In a further two steps (*1b*,*1c*), which are considered to be very rapid as compared with the first step (*1a*), it is assumed that β-elimination of methanol from the 2,3-dimethoxyl-propen-1-ol (*1b*) occurs, followed by final hydrolysis of 2-methoxypropenal to form 2-oxopropanal (*1c*), In the second step, it is possible that hydrolysis of the corresponding enol ether conducted in deuterated medium, would lead to incorporation of deuterium into the hydroxymethyl group of the 2-oxo-3-methoxy-1-propanol produced, which would also appear in the aldehyde group of the final

2-oxopropanal. As this incorporation does not occur, it is assumed that β-elimination of the protonated methoxyl group at C-3 of the 2,3-dimethoxy-1-propen-1-ol molecule is much faster than the hydrolysis considered. This asertion is also in agreement with the finding that aqueous 3-ethoxy-2-cyclohexenol with solutions of hydrochloric acid do not lead to 3-hydroxycyclohexanone but only to 2-cyclohexenone[28]. It may be assumed, as demonstrated later, that β-elimination of the protonated methoxyl group at C-3 in the 2,3-dimethoxy-1-propen-1-ol molecule is the driving force for this reaction, and that dissociation of a proton from the hydroxyl group at C-1 does not play an important role in this process. The third step in this reaction (*1c*) corresponds to acid-catalyzed hydrolysis of 2-methoxypropenal through the same mechanism as was demonstrated in detail for similar types of vinyl ether[19]. It is known that the hydrolysis of vinyl ethers is generally acid-catalyzed, and that the rate-determining step is proton transfer from the catalyzing acid to the substrate with formation of the resonance-stabilized, oxonium–carbonium cation. In this step, incorporation of deuterium into the methyl group of the 2-oxopropanal produced occurs. It should be noted that, under the conditions described, deuterium is also incorporated directly into the 2-oxopropanal formed[18,29], so that it is relatively rather difficult to determine the relation of these two reactions in the overall incorporation. It is evident that, according to this mechanism, incorporation of only one deuterium atom into the 2-oxopropanal, and further deuterium atoms into the 2-oxopropanal being formed, took place.

It is suggested in the proposed mechanism (*1a*) that the enolization of 2,3-di-*O*-methyl-D-glyceraldehyde is preceded by protonation, with formation of the corresponding mesomeric forms. It seems that a more-realistic picture is yielded by quantum-chemical calculation of the electronic and geometric structures of this protonated molecule (Fig. 4, structures **1**, **1a**, **2**, and **2a**). Delocalization of the positive charge over the whole molecule stabilizes the protonated form and leads to a marked redistribution of charge as compared with the unprotonated forms. From the point of view of enolization, the considerable relative increase in the acidity of the hydrogen atom in the C–H bond on the α-carbon atom with respect to the carbonyl group is important; dissociation of this hydrogen atom leads to formation of the enol form, namely, 2,3-dimethoxy-1-propen-1-ol. Similarly, the experimentally determined, retarding effect of the methoxyl group in the enolization rate is in agreement with the calculated decrease in the positive charge, that is, the acidity of the α-hydrogen atom in the 2,3-di-*O*-methyl-D-glyceraldehyde molecule as compared with unsubstituted D-glyceraldehyde (Fig. 4, structures **1** and **2**). The alternative possibility of hydrolysis of 2,3-dimethoxy-1-propen-1-ol already rejected is unambiguously explained by the electronic charge-distribution in this molecule (Fig. 4, structure **2b**). The marked negative charge on the lone electron-pair of the oxygen atom in the methoxyl group at C-3, as compared with the positive charges localized on the carbon atoms forming the double bond, indicate quite clearly that the donor properties of the oxygen and carbon atoms in the 2,3-dimethoxy-1-propen-1-ol molecule are different. It follows unambiguously from the charge values that the proton will be bonded preferentially



to the oxygen atom, leading to elimination of methanol with formation of 2-methoxypropenal.

Similarly, on the basis of the experimental data obtained and in agreement with the theoretical data, the following mechanism is proposed for the acid-catalyzed formation of 2-oxopropanal from 1,3-dimethoxy-2-propanone.

The reaction process thus consists (in principle) of two steps, enolization of 1,3-dimethoxy-2-propanone (**2a**) and β-elimination of the protonated methoxyl group from the enol ether formed, that is, from 1,3-dimethoxy-2-propenol, with formation of the corresponding oxonium–carbonium cation which, after acid-catalyzed addition of water and elimination of methanol, yields 2-oxopropanal as a final product (**2b**) Enolization of 1,3-dimethoxy-2-propanone is also considered as the slowest and generally acid-catalyzed step in the reaction (**2a**), in agreement with the foregoing discussion. Interestingly the values of the rate constants and activation energies for the acid-catalyzed reactions of 1,3-dihydroxy-2-propanone[17] and its methylated derivative are practically identical (Table I), indicating that the factors affecting the kinetics are contrary and eliminate one another. Thus, for example, the effect of the two methyl groups in the α-position relative to the carbonyl group in the 1,3-dimethoxy-2-propanone molecule increases the basicity of the latter, making its protonation easier; on the other hand, these methyl groups decrease the acidity of the hydrogen atoms on neighboring carbon atoms and thus decrease their dissociability (Fig. 4, structures **3** and **4**). β-Elimination of methanol from the protonated 1,3-dimethoxy-2-propenol, producing the resonance-stabilized cation, is the driving force for this reaction (**2b**). The easier hydrolizability of 1,3-dihydroxy-2-propanone and its methylated derivative indicates that the presence of a dissociable proton on the free hydroxyl group at C-1 is not necessary for these types of reaction to occur. Similarly, β-elimination reactions of the allyl type[30] are observed frequently in the chemistry of saccharides and their derivatives. They are important, for example, in the formation of 2-furaldehyde from 2,5-anhydro sugars[5], in the conversion of glycals

into gly-2-enoses[31] and in the formation of 2-furaldehydes from 2-hydroxyglycals[32], and of levulinic acid from furfuryl alcohol[5].

The much higher rate of acid-catalyzed hydrolysis of 1,3-dihydroxy-2-propanone and its methylated derivative, as compared with that for the hydrolysis of glyceraldehyde and its methylated derivative, completely eliminates the alternative possibility of hydrolysis of 1,3-dimethoxy-2-propenol. This reaction would lead to formation of 3-methoxy-DL-glyceraldehyde, whose necessary enolization would be the slowest step in the whole reaction process. The conformation and electronic structures of the protonated form of 1,3-dimethoxy-2-propanone and 1,3-dimethoxy-2-propenol (Fig. 4, structures **4a.4b**) lead to the same conclusions as found for the analogous compounds of D-glyceraldehyde.

It may be considered to be demonstrated that the acid-catalyzed reactions of methylated trioses proceed only through the enol forms, which are different and thus cannot constitute the same intermediates in the formation of 2-oxopropanal as possible with unsubstituted trioses. In some direction, these data might throw some light on the mechanism of dehydration of free trioses; nevertheless this proposal should be carefully interpreted because of a possible different reaction course[18].

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