A QUANTUM-CHEMICAL STUDY OF DEHYDRATION
OF ORTHO FORMS OF FORMALDEHYDE AND FORMIC ACID

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Gas-phase dehydration of methanediol (*I*) and methanetriol (*II*) has been studied by the MINDO/3 method with full optimization of the reaction paths. The intramolecular dehydration goes *via* high barriers (*I* 257·4, *II* 193·3 kJ mol^{-1}). The acid-catalyzed dehydration involving protonation at oxygen atom of *I* goes *via* a considerably lower barrier (63·3 kJ mol^{-1}), whereas protonation at oxygen atom of *II* results in practically spontaneous dehydration (0·4 kJ mol^{-1}), which is the reason for the formic acid not being hydrated in water. Deprotonation of the protonated formaldehyde (*III*) and protonated formic acid (*IV*) is connected with high barriers (429·1 and 523·0 kJ . . mol^{-1}, resp.). The deprotonation by a water molecule added to *III* and *IV* involves substantially lower barriers (53·9 and 96·3 kJ mol^{-1}, resp.).

Formaldehyde dissolved in water is hydrated to methanediol according to the equation $CH_2O + H_2O \rightarrow CH_2(OH)_2$, the reaction half-life[1,2] being of the order of 10^{-1} s. The reaction is reversible, the equilibrium constant (of thede hydration) being of the order of 10^{-4} (25°C) (ref.[3]). Hence, only about 1% of the molecules are not hydrated in water. The addition reactions of nucleophiles to formaldehyde in aqueous media involve the dehydration of methanediol as the rate-limiting step[1]. There exists a number of experimental studies[4] dealing with hydration and dehydration of formaldehyde. On the other hand it is not known that formic acid would be hydrated to the ortho acid in aqueous media, but the corresponding ortho esters are stable and undergo acid- or base-catalyzed hydrolysis in water[5]. This hydrolysis should produce the free ortho acid. It is presumed, however, that as soon as after hydrolysis of the two alkoxy groups a water molecule is split off to give the carboxylic acid ester.

From the facts given it is obvious that there exists a substantial difference in stabilities of the ortho forms of formaldehyde and formic acid which is due to their electronic structure. The hydration mechanism of formaldehyde and structure of the gas-phase transition state are dealt with in the quantum-chemical studies[6,7]. But, as far as we know, the dehydration mechanisms of methanediol and methanetriol have not been studied quantum-chemically yet. Therefore, we have carried out such a study using the semiempirical MINDO/3 method with full optimization of the reaction paths.

CALCULATIONS AND DISCUSSION

The molecular geometries of methanediol and methanetriol were fully optimized. Their parameters are given in Table I, and the projections of models are presented in Fig. 1.

The energetically most favourable geometry of methanediol belongs to the C_2 symmetry group (the *sc, sc* conformation) with the angles of deviation of hydrogen atoms equal to 55·8° in accordance with the results of *ab initio* calculations[6,8,9]. The CO bond length value, however, is lower than that of the *ab initio* calculations[8] by as much as 0·0058 nm, the difference being even greater according to ref.[6]. This is an immanent property of the MINDO/3 method in the case of bond lengths between atoms with free electron pairs[10]. Similarly, longer CH bonds as well as smaller bond angle between them represent an artifact of the MINDO/3 method[11].

TABLE I

The geometry parameters[a] of methanediol and methanetriol in the intramolecular dehydration at the beginning of the reaction and in its transition state

CH₂(OH)₂		Transition state		CH(OH)₃		Transition state	
R_{CH}	0·1139	R_{CH}	0·1134	R_{CH}	0·1151	R_{CH}	0·1147
R_{CO}	0·1358	R_{CO^3}	0·1445	R_{CO}	0·1379	R_{CO^3}	0·1437
R_{OH}	0·0951	R_{CO^5}	0·1302	R_{OH}	0·0950	R_{CO^5}	0·1358
∢H¹CO⁵	101·0	$R_{O^3H^4}$	0·0956	∢HCO	102·8	R_{CO^7}	0·1359
∢H¹CO³	112·8	$R_{O^5H^6}$	0·1021	∢COH	117·8	$R_{O^3H^4}$	0·0959
∢COH	114·5	∢H¹CO⁵	119·6	∢O³CO⁵	115·3	$R_{O^5H^6}$	0·0952
∢HCH	106·2	∢H¹CO³	110·1	∢HCO³H⁴	240·6	$R_{O^3H^8}$	0·1200
∢OCO	122·3	∢H⁷CO³	125·8	∢HCO⁵H⁶	240·6	∢HCO³	109·9
∢H¹CO⁵H⁶	181·3[b]	∢CO⁵H⁶	88·2	∢HCO⁷H⁸	188·7	∢HCO⁵	99·9
∢OCOH	55·8	∢HCH	103·9			∢HCO⁷	114·4
		∢CO³H⁴	137·3			∢CO³H⁴	117·6
		∢O⁵CO³	77·2			∢CO⁵H⁶	117·6
		∢H¹CO⁵H⁶	103·8			∢CO⁷H⁸	79·2
		∢H⁴O³CH⁷	59·5			∢O³CO⁷	90·0
		∢H⁴O³CH¹	294·1			∢O³CO⁵	122·7
		∢O³CO⁵H⁶	19·0			∢O⁵CO⁷	120·6
		∢O⁵CO³H⁴	176·9			∢HCO⁵H⁶	188·7
						∢HCO⁷H⁸	112·0
						∢HCO³H⁴	188·7
						∢CO⁷H⁸O³	0

[a] The bond lengths and angles are given in nm and degrees, resp. [b] The dihedral angles are defined in the way used in the MINDO/3 program.

The OCO angle is greater by as much as 11° than that of the *ab initio* calculations[6,12,13]. It must be mentioned, however, that in the *ab initio* calculations the geometries were not optimized by the gradient method, but were optimized numerically and — in some cases — only partially with the use of the standard values[14] for some parameters. The fully optimized MINDO/3 geometry is noteworthy by its having both its OH bonds in antiperiplanar positions to the corresponding CH bonds. There are two pairs of HCO angles. The bond angles in the coplanar quartets of atoms are greater (112·8°) and those of the other pair are smaller (101·0°) than the angle of an sp^3 hybridized carbon atom. The optimum geometry of methanetriol corresponds to the *tgg* conformation, the OH groups being rotated by 60° to the gauche position (Table I), which agrees with the *ab initio* calculations[9]. The third OH group is not precisely in the *t* position but is slightly deviated to the *g* position (by 8·7°). The COH angles in methanediol (114·5°) and methanetriol (117·8°) are greater than that found experimentally[15] in methanol (110°).
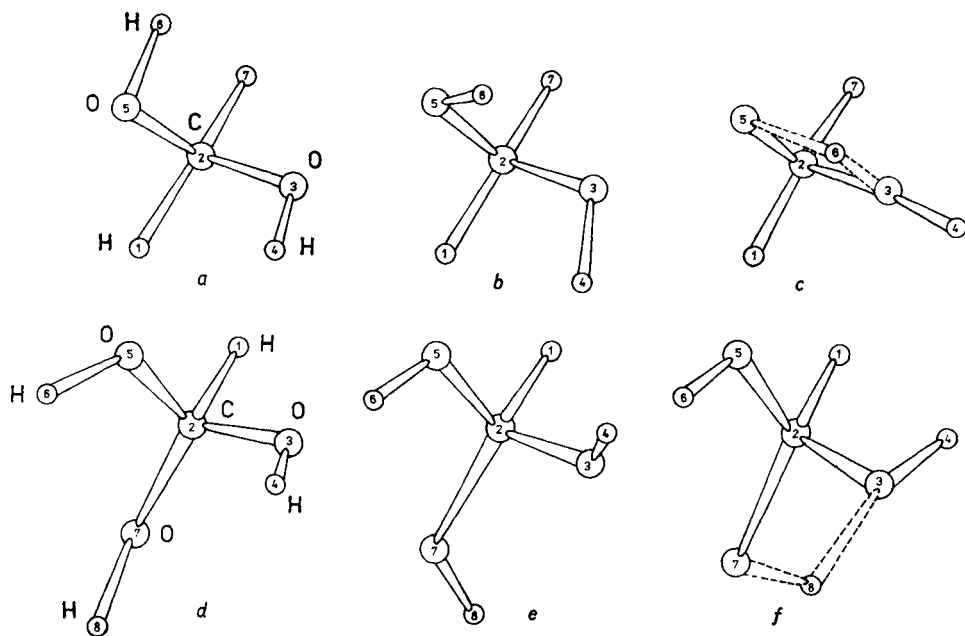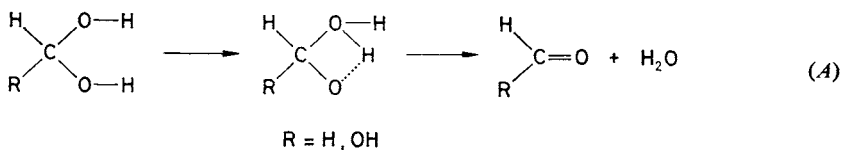

FIG. 1

The models of methanediol and methanetriol on the reaction path during intramolecular dehydration. *a, d* — at the beginning of the reaction; *b, e* — on the reaction path before the barrier; *c, f* — the transition state

INTRAMOLECULAR HYDROGEN TRANSFER

The first step of our study concerned the intramolecular hydrogen transfer in the isolated molecules according to Eq. (A) which corresponds to the gas-phase reactions.

Dehydration of methanediol. We started from the optimized geometry of the *sc, sc* conformer (Fig. 1). In the reaction (A) the distance between H^6 hydrogen and O^3 oxygen represents the reaction coordinate R_{63}. The starting value $R_{63} =$

$$
\begin{array}{ccc}
\underset{R}{\overset{H}{\diagdown}}C\overset{O-H}{\underset{O-H}{\diagup}} & \longrightarrow & \underset{R}{\overset{H}{\diagdown}}C\overset{O-H}{\underset{O}{\diagup}}H & \longrightarrow & \underset{R}{\overset{H}{\diagdown}}C=O \;+\; H_2O
\end{array}
\tag{A}
$$

$$R = H, OH$$

$= 0.2664$ nm of the equilibrium conformation was lowered by 0.01 nm steps down to the final value of 0.1000 nm, and, after each R_{63} value, the energy of the system was minimized with respect to all other coordinates*. The hydrogen transfer according to (A) represents an $[1, 3]$ shift, which is symmetry-forbidden, and, therefore, it should go through a barrier. According to Fig. 2a, the decreasing of the reaction coordinate is really connected with an energy increase. At the same time the CO^3
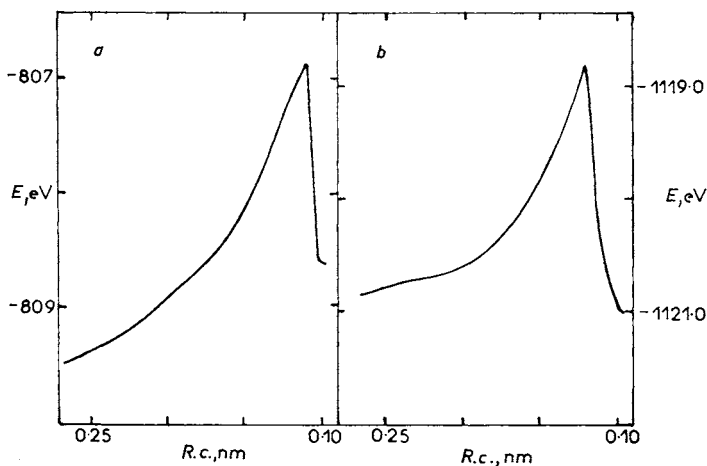

FIG. 2

The reaction paths of intramolecular dehydrations of methanediol (a) and methanetriol (b)

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*   In all the subsequent calculations of the reaction paths the reaction coordinate was lowered by 0.01 nm steps.

bond is lenghtened and the CO^5 bond is shortened. About the reaction coordinate value of 0.16 nm the energy begins to increase steeply, and it attains — by an almost linear course — the energy barrier at $R_{63} = 0.11$ nm. The O^5H^6 and CO^3 bonds being split were lenghtened to 0.1021 and 0.1445 nm, resp. Further decrease of the reaction coordinate results in an abrupt energy decrase accompanied by a distinct change in structure and electron distribution. The structure of methanediol collapsed, and structures of formaldehyde and water were formed. This fact is obvious from the values of parameters: after the optimization the newly formed O^3H^6 bond has the length of 0.0949 nm which corresponds to the OH bond length of water[10]. The CO^3 bond was split, as seen from the length of 0.5159 nm, and the CO^5 bond length decreased to the CO bond length value of carbonyl group 0.1182 nm (exp. 0.1210 nm)[16]. The energy barrier is 257.4 kJ mol^{-1}.

The transition state possess a geometry of apparent symmetry of C_s' group. In reality the geometry is slightly deformed. The quadrangle $O^3CO^5H^6$ is not planar ($\angle O^3CO^5H^6 = 19°$), and the O^3H^4 bond is slightly deviated from the apparent plane of the quadrangle. Similarly the CH^1 and CH^7 bonds do not include symmetrical bond angles.

The electron distribution was changed relatively little. The O^3, O^5 oxygen atoms became less negative, whereas the carbon became less positive. Only the transferred H^6 hydrogen atom changed substantially its positive charge (from 0.266 to 0.100), which reflects its tendency to remain in the electron system of the molecule.

Dehydration of methanetriol. The treatment started from the optimized *tgg* conformer (Fig. 1), the interatomic distance H^8—O^3 representing the reaction coordinate R_{83}. The starting value $R_{83} = 0.2652$ nm was diminished to the final value of 0.10 nm. In this case, too, the reaction goes through a barrier (Fig. 2b), the energy being — at first — slowly increasing up to $R_{83} = 0.20$ nm wherefrom it begins to increase rapidly and — in an almost linear course — attains the barrier at $R_{83} = 0.12$ nm. Further decrease of the reaction coordinate results in an abrupt energy decrease with simultaneous collapse of the methanetriol structure and formation of the molecules of formic acid and water. This is indicated by the splitting of the O^7H^8 and CO^3 bonds as well as by the change of the CO^7 bond into the CO bond of carboxyl group. After the energy minimization of the system at $R_{83} = 0.10$ nm the O^7H^8, CO^3, and CO^7 bond lengths are 0.4830, 0.4177, and 0.1204 nm, resp. The energy barrier is somewhat lower than that in the previous case (193.3 kJ mol^{-1}).

The transition state has a geometry without symmetry (C_1). The CO^3 and O^7H^8 bonds are considerably stretched, which indicates their weakening and subsequent rupture. The HCO^3, HCO^7, O^3CO^5, and O^5CO^7 angles, in each of which one bond is involved in the four-membered cycle, are considerably increased, which is connected with the strain accompanying the formation of quadrangle. The other bond

lengths and angles, which are not involved in the formation of the cycle, are changed but little. Surprisingly, the four-membered ring is planar ($\sphericalangle CO^7H^8O^3 = 0°$). The O^5H^6 bond, which was originally at the gauche position, is now in antiperiplanar position with respect to the CH^1 bond.

Most atoms have their charge distribution changed relatively little. Also in this case the carbon atom became less positive, but the O^7 and O^3 oxygen atoms, which form a part of the cycle, became more negative, and the H^8 hydrogen transferred became more positive. This situation is opposite to that of methanediol, and it can be explained by the mesomeric effect of the O^5H^6 hydroxyl group. The oxygen atom of this group became − on the contrary − less negative in the transition state. Thus a charge delocalization took place in the transition state on the atomic triad O^5CO^7 (through the empty orbital being formed at the carbon atom) and − to a lesser extent − on the triad O^5CO^3, too. The mesomeric stabilization of concentra tion of electrons at these triads results in a decrease of electron density at the H^8- hydrogen atom (the net charge up to $+0.370$). So this hydrogen is weakly bound. Its weak bond also explains why the four-membered ring $CO^7H^8O^3$ is not distorted in space, as it is the case with methanediol, in which the hydrogen atom has a much lower net charge ($+0.100$).

The mechanism presumed can only operate in vacuum. Real media of nucleophilic substitutions are predominantly aqueous. The study[17] of hydration of formaldehyde showed that addition of a cluster of water molecules will decrease the energy barrier without affecting the mechanism. Therefore, the aqueous medium was simulated by addition of a cluster of water molecules in such a way that a closed cycle might be formed between the hydrogen transferred and the migration terminal. Unfortunately, the MINDO/3 method is unable to describe such a cluster, and the water molecules show repulsive behaviour.

The slower energy increase as well as lower barrier of methanetriol can be explained by the above-mentioned mesomeric stabilization of the positive charge formed at the carbon atom after splitting off of water by the remaining hydroxyl group. This is obviously also connected with the fact that the dehydration of methanetriol is exothermic, whereas that of methanediol is endothermic (Fig. 2).

ACID-CATALYZED DEHYDRATION

From the above text it follows that dehydration of both methanediol and methanetriol by intramolecular rearrangement of hydrogen proceeds *via* a high barrier. According to what was presumed, this barrier can be lowered by solvation in aqueous medium. However, also in this case it will be quite high because of the forbidden [1, 3] shift involved. According to an intuitive idea, the water molecule can be removed by protonation of the hydroxyl group, splitting off of a water molecule, and deprotonation according to Eq. (*B*).

$$R = H, OH$$

(B)
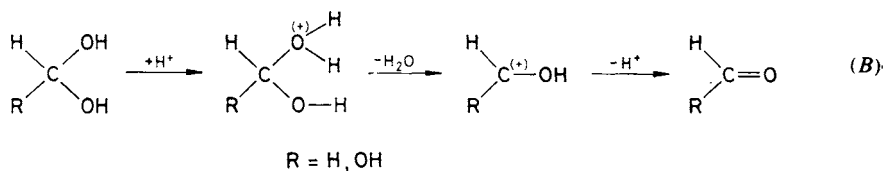
Protonation of Methanediol and Methanetriol and Deprotonation of Formaldehyde and Formic Acid

Methanediol. According to Fig. 3 the proton was added to the structure with the geometry of *sc, sc* conformation, and the system was optimized. The protonation at O^3 oxygen results in lenghtening of CO^3 bond from 0·1358 nm to 0·1479 nm and shortening of CO^5 bond from 0·1358 nm to 0·1301 nm. The CH and OH bond lengths are changed but little. Considerably increased are the bond angles HCH (from 105·7° to 113·4°) and CO^5H^6 (from 114·5° to 118·9°) (Table II), which indicates rehybridization at C and O^5 from sp^3 to sp^2.
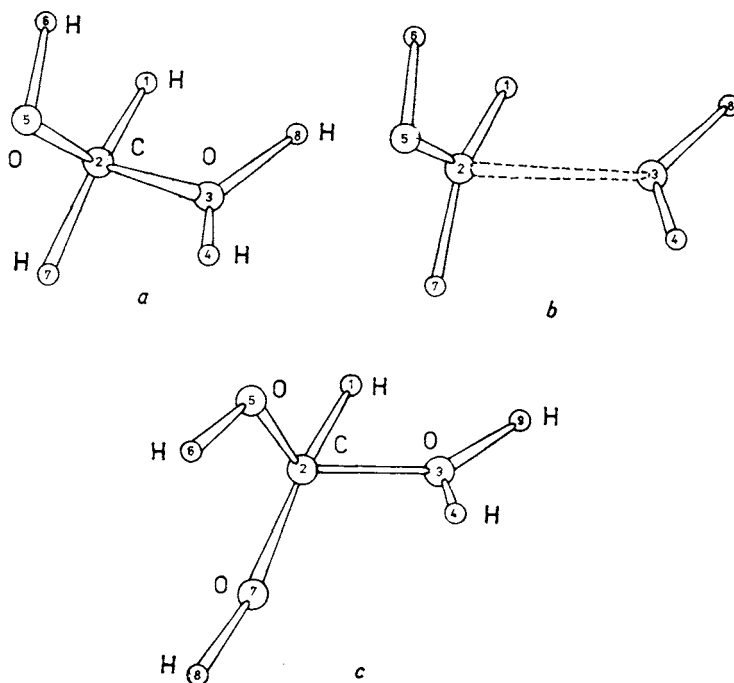

FIG. 3

The model of the protonated methanediol (*a*) and methanetriol (*c*)

A comparison of the geometry parameters with the *ab initio* values[6] shows a good agreement for the bond lengths except CO^3 which — according to the *ab initio* calculation — is longer by as much as 0·02 nm. Some bond angles agree well, too, but others show considerable deviations.

A peculiarity of the structure of the protonated form consists in that the O^3H and CO^3 bonds are coplanar. The CH^1 and C^3H^4 bonds are mutually antiperiplanar as in methanediol, hence the O^3H^4 bond is at gauche position to CO^5. On the contrary, the O^5H^6 bond was changed from the antiperiplanar arrangement with the CH^7 bond to the gauche position with respect to this bond. It also remains in gauche position with respect to the CO^3 bond, but the deviation angle was increased to 92·4°.

The protonation also results in a change of electron distribution. The O^5 atom became less negative and O^3 even less negative. The C atom became less positive, whereas the H^6 and H^4 atoms became more positive. The H^1 and H^7 atoms, which were negatively charged in methanediol, became positive.

The dehydration was realized by stepwise splitting off of H_2O from the protonated methanediol *via* the optimized reaction path. The choice of the reaction coordinate

TABLE II

The geometry parameters[a] of the protonated forms of methanediol and methanetriol in the dehydration at the beginning of the reaction and in its transition state

$CH_2(OH)(OH_2)^+$		Transition state	$CH(OH)_2(OH_2)^+$	
R_{CH}	0·1128[b]	0·1112	R_{CH}	0·1138
R_{CO^3}	0·1479	0·2200	R_{CO^3}	0·1655
R_{CO^5}	0·1301	0·1233	$R_{CO^{5,7}}$	0·1307
R_{O^3H}	0·0960	0·0953	$R_{O^3H^{4,5}}$	0·0957
R_{O^5H}	0·0955	0·0958	$R_{O^{5,7}H^{6,8}}$	0·0955
∡HCH	113·4	120·3	∡OCH	108·6
∡OCO	98·1	76·3	∡COH	123·2
∡OCH	117·3	124·5	∡HCO^3H^9	0
∡COH	118·9	123·6	∡HCO^3H^4	180·0
∡$H^1CO^3H^4$	180·0	180·0	∡HCO^5H^6	166·9
∡$H^1CO^3H^8$	0	0	∡HCO^7H^8	192·0
∡$H^1CO^5H^6$	325·9	357·1		
∡$H^7CO^5H^6$	196·2	182·5		
∡$H^4O^3CO^5$	233·5	237·5		
∡$H^6O^5CO^3$	92·4	111·9		

[a] The bond lengths and bond angles are given in nm and degrees, resp. [b] The bond lengths of hydrogen atoms differ in the fifth decimal.

is seen from Fig. 3b. The starting value $R_{23} = 0.1479$ nm was gradually lenghtened up to the final (already non-bonding) distance of 0.300 nm. The dependence of the system energy on the reaction coordinate (Fig. 4a) shows that the dehydration of the protonated form goes *via* a barrier which is substantially less steep than that of the intramolecular dehydration. The energy only increases steeply in the initial phase, which indicates a relatively stable complex. Also relatively more stable is the activated complex on the barrier which is reached at the value of $R_{23} = 0.2200$ nm and is relatively flat. The model of the activated complex is given in Fig. 3, and its geometry parameters are presented in Table II. The energy barrier is 63.3 kJ mol^{-1}.

The geometry of the transition state was changed relatively little except for the HCH angle which increased to a value very close to that of formaldehyde. The CO^5, CH^1, CH^7 bonds arranged to a very flat pyramid close to a plane. The CO^{5}H^6 angle increased to the value corresponding to the sp^2 hybridized oxygen atom.

The electron structure was considerably changed on the O^3 oxygen which became much more negative and on the O^5 oxygen which — on the contrary — became less negative. The carbon atom became more positive. The changes on the other atoms are relatively small.

As the proton acts as a catalyst, it must be released after the dehydration. Therefore, we carried out a calculation of the deprotonation of formaldehyde by a simple splitting off of the proton *via* the optimized path, which can be realized by vibrational
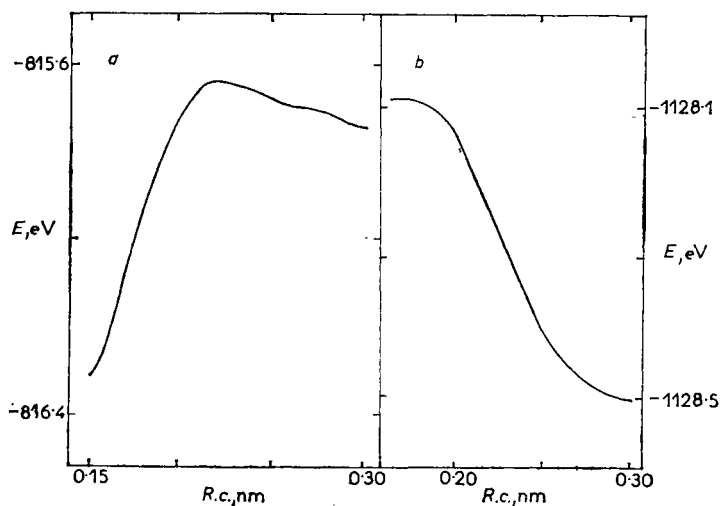

FIG. 4

The reaction paths of dehydration of the protonated methanediol (*a*) and protonated methanetriol (*b*)

motions. The reaction coordinate is represented by the O^5H^6 bond. Its gradual increase is connected with a steep energy increase of the system, the course being almost linear, and the barrier is reached at the value of the reaction coordinate 0·18 nm. Further increasing of the reaction coordinate results in an abrupt decrease of energy and rupture of the O^5H^6 bond. The barrier is huge (429·1 kJ mol^{-1}) and is equal to the OH bond energy. In a real medium (mainly aqueous) the barrier can be lowered by solvation of the reacting system. Modelling of this mechanism is dealt with in a special paragraph.

Methanetriol. Attachment of the proton to the *tgg* conformation according to Fig. 3 after the optimizing results in a lengthening of CO^3 bond from 0·1379 nm to 0·1655 nm, which indicates a weakening of the bond. The CO^5 and CO^7 bonds are shortened from 0·1379 nm to 0·1307 nm. The CO^5H^6 and CO^7H^8 angles are increased from 117·8° to 123·2°. Also the HCO^3 and HCO^5 angles are increased from 102·8° to 108·6°, which indicates rehybridization at the carbon and oxygen atoms. The O^3H^4 bond is antiperiplanar to the CH bond. The O^5H^6, O^7H^8 bonds are only little deviated to the gauche position. The O^3H^9 bond is coplanar with the CO^3 and O^3H^4 bonds here, too.

The electron density was considerably changed particularly at the oxygen atoms which became more negative, the O^3 and O^5 atoms being the most and the least negative, resp. All the hydrogen atoms became more positive.

For the dehydration we chose the reaction coordinate according to Fig. 3 with the starting value $R_{32} = 0·1655$ nm. With increasing R_{32} the energy of the system increases but slightly and, having reached a low and flat barrier near 0·1800 nm, it decreases quite rapidly (Fig. 4b). The value of the barrier is only 0·4 kJ mol^{-1}.

TABLE III

The geometry parameters[a] of the protonated forms of formaldehyde and formic acid

	C^+CH_2OH		$C^+H(OH)_2$
R_{CH}	0·1110[b]		0·1127
R_{CO}	0·1223		0·1264
R_{OH}	0·0959		0·0956
∢HCH	118·7	∢HCO	111·7
∢OCH^1	126·2	∢COH	125·8
∢OCH^7	115·1	∢OCO	136·3
∢COH	121·8		

[a] The bond lengths and angles are given in nm and degrees, resp. [b] The R_{CH^1} and R_{CH^7} values differ in the fifth decimal.

The energy changes are accompanied by structural changes leading to the protonated formic acid. After splitting off of the water molecule, the CO^5, CO^7 bond lengths are further shortened from 0·1307 nm to 0·1264 nm. The CH and OH bonds are changed but slightly. Considerably increased are the angles O^5CH^1, O^7CH^1 (from 108·6° to 112·0°) and CO^5H^6, CO^7H^8 (from 123·2° to 125·8°). The dehydration of the protonated methanetriol is thus substantially different from that of the protonated methanediol in being practically without barrier, because the low value given is easily surpassed by vibrational motions at room temperature. This confirms correctness of the presumption[5] that a water molecule is split off after hydrolysis of two alkoxy group of orthoester of carboxylic acid. The splitting is still easier than that of the model example of methanetriol with respect to the greater $+I$ effect of the remaining alkoxy group.

Similarly we carried out a calculation of the optimized reaction path of deprotonation of the protonated form of formic acid which remains as a stable system after splitting off of the water molecule. The O^7H^8 bond represents the reaction coordinate (Fig. 3). Its gradual increase from the starting value $R_{78} = 0·0956$ nm is connected with a steep energy increase (Fig. 5b) similar to that of the protonated formaldehyde, and the barrier is reached near the value of $R_{78} = 0·20$ nm. Thereafter a slight increase of the reaction coordinate causes an abrupt energy decrease indicating the bond rupture. The energy barrier is even higher than that of the protonated formaldehyde (523·0 kJ mol^{-1}), which can be explained by mesomeric stabilization of the
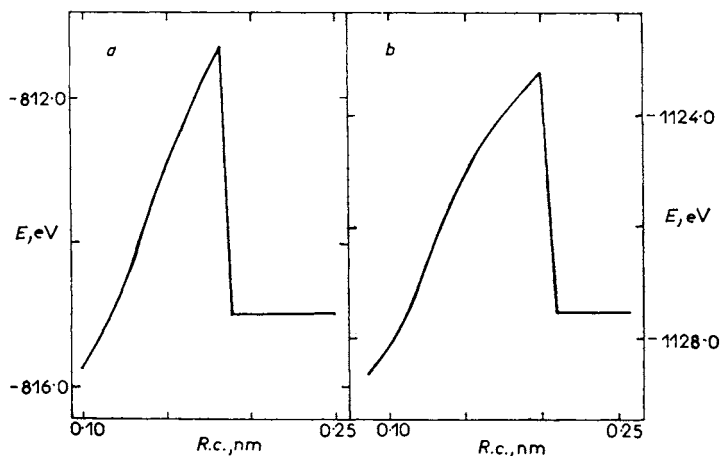

Fig. 5

The reaction paths of deprotonation of the protonated formaldehyde (a) and protonated formic acid (b) (the geometry parameters see Table III)

positive charge at the carbon atom by the remaining hydroxyl group. The mesomeric effect on the bond strength is also indicated by the greater curvature on the increasing section of the reaction path of protonated formic acid (Fig. 5b) and by the greater extent of bond stretching as compared with that of the protonated formaldehyde (the reaction coordinate of the bond rupture is 0·18 nm and 0·20 nm with C^+H_2OH and $C^+H(OH)_2$, resp.). The curvature is connected with the decrease of the mesomeric effect due to withdrawal of the proton from the oxygen atom of formaldehyde or formic acid.

Effect of Aqueous Medium on the Deprotonation Reaction Paths

The aqueous medium was modelled by addition of one water molecule to the protonated molecule of formaldehyde or formic acid. The system was optimized to give an associate, and in the subsequent step the H_3O^+ ion was split off which formed then an associate with formaldehyde or formic acid according to Eq. (C).

$$(C)$$

R = H, OH
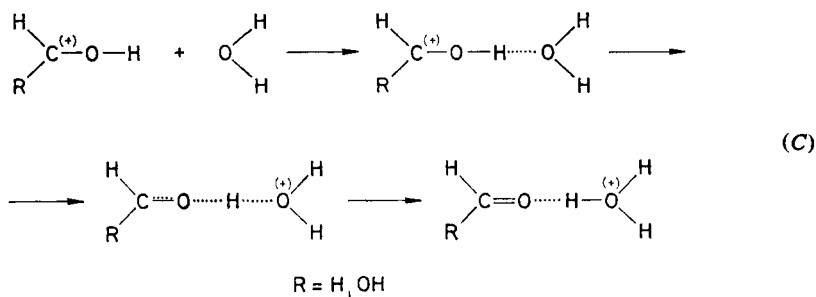
Protonated formaldehyde. The MINDO/3 method is known to be unable to describe a hydrogen bond between water and carbonyl compounds[18]. This method, however, provides a defined associate between the protonated formaldehyde and water with the stabilization energy of $-20·0\ \text{kJ mol}^{-1}$. Its spatial arrangement is presented in Fig. 6a. After formation of the associate the geometry parameters of the protonated formaldehyde are changed but slightly. The position of water with respect to the protonated formaldehyde is determined unambiguously by the distance $R_{56} = 0·3117$ nm and by the dihedral angles $CO^3H^5O^6$ 180·5°, $O^3H^5O^6H^7$ 105·4°, and $O^3H^5O^6H^8$ 254·0°. The value of $CO^3H^5O^6$ dihedral angle indicates that the O^6H^5 bond, which forms the associate, lies in the plane of the protonated formaldehyde, because the $H^1CO^3H^5$ dihedral angle is also 180·0° (the CH^4 bond is only little deviated from the plane). The reaction coordinate is the R_{35} interatomic distance. The original O^3H^5 bond length of 0·1017 nm was gradually lengthened. From Fig. 7a it can be seen that the energy steeply increases at first (up to $R_{35} = 0·12$ nm), whereafter it increases more slowly and reaches the barrier at $R_{35} = 0·1900$ nm.

Thereafter the energy decreases only slightly to reach the minimum at $R_{35} =$ $= 0.2400$ nm which is shallow but perceptible. The interrupted section of the curve indicates a worsened convergence of the optimization procedure. The height of the barrier is 53.9 kJ mol^{-1}. The energy of removal of the H_3O^+ ion to infinity equals
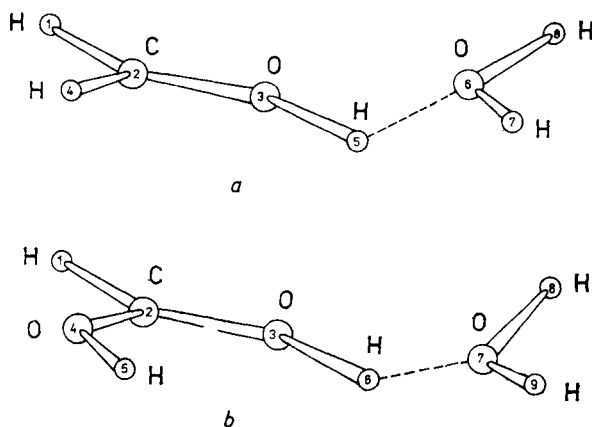

FIG. 6

The models of the associates of the protonated formaldehyde with water (*a*) and of the protonated formic acid with water (*b*)
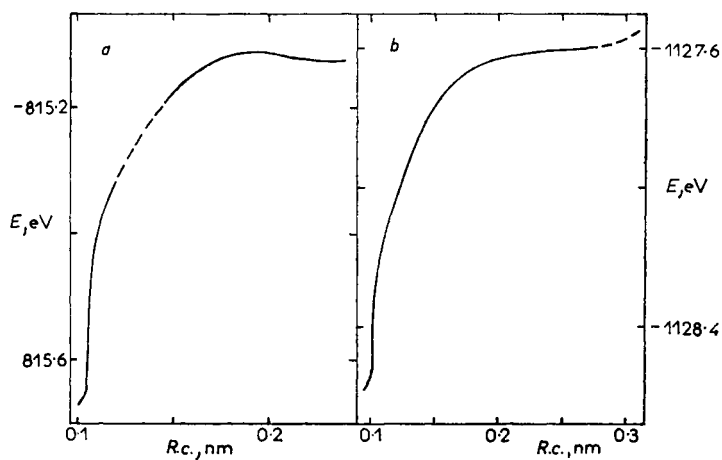

FIG. 7

The reaction paths of deprotonation of the protonated formaldehyde (*a*) and protonated formic acid (*b*) with participation of water

its association energy with formaldehyde, *i.e.* $-29 \cdot 7 \, \text{kJ mol}^{-1}$. Hence the first barrier is higher, but it represents only a fraction of the barrier found in gas phase.

On the barrier the H^5-O^6 distance is $0 \cdot 0982 \, \text{nm}$, which is only slightly more than in the minimum ($0 \cdot 0969 \, \text{nm}$). The associated H_3O^+ ion has a shape of a pyramid with the HO^6H angle $109 \cdot 1°$ (in the isolated ion $109 \cdot 4°$) which is close to the value ($111 \cdot 3°$) measured[19]. The shift of H^5 hydrogen atom to the second minimum of the hydrogen bond caused certain changes in the electron distribution. The charge transfer mainly took place at the O^3, O^6, H^5, H^8 atoms: O^3 became more negative than O^6, and H^8 became more positive than in the first minimum, which agrees with the character of the oxygen bonds.

The protonated formic acid. The MINDO/3 method also gives a defined associate for the protonated formic acid and water with the stabilization energy of $-15 \cdot 9 \, \text{kJ}$. $. \text{mol}^{-1}$. The position of water with respect to the protonated formic acid in the optimized associate can be seen in Fig. 6b. It is unambiguously determined by the interatomic distance $R_{67} = 0 \cdot 3067 \, \text{nm}$ and by the dihedral angles $CO^3H^6O^7 \, 144 \cdot 7°$, $O^3H^6O^7H^8 \, 3 \cdot 1°$, and $O^3H^6O^7H^9 \, 176 \cdot 0°$. From the values given it is obvious that the O^3H^6 bond lies approximately in the plane of the water molecule.

The reaction coordinate is represented by the O^3H^6 interatomic distance. From Fig. 7b it is obvious that increasing of the starting value $R_{36} = 0 \cdot 0960 \, \text{nm}$ is connected with a rapid energy increase (indicating a stable associate) up to $R_{36} = 0 \cdot 18 \, \text{nm}$, whereafter the energy increases slowly and attains the barrier at about $R_{36} \sim 0 \cdot 27 \, \text{nm}$. Then there should follow a minimum, it is, however, indistinct due to worsened convergence of the optimization procedure. Its position should be in the region indicated by the interrupted line. The height of the barrier is $96 \cdot 3 \, \text{kJ mol}^{-1}$. It is higher than the association energy of the H_3O^+ ion with formic acid (about $-39 \, \text{kJ mol}^{-1}$) and represents also only a fraction of the value found in gas phase.

On the barrier the interatomic distance H^6-O^7 is $0 \cdot 0967 \, \text{nm}$. In the minimum (which is near $R_{36} = 0 \cdot 29 \, \text{nm}$) this distance is presumed to be only slightly less, as it is also in the case of formaldehyde.

Also here the barrier of formic acid is higher than that of formaldehyde, and the bond is stronger, which is also indicated by its greater stretching ($0 \cdot 19 \, \text{nm}$ and $0 \cdot 27 \, \text{nm}$). The reason is the same as in gas phase.

In conclusion it can be stated that gas-phase intramolecular dehydrations of methanediol and methanetriol proceed through high barriers, that of the methanetriol being lower. The protonation of methanediol results in a substantial lowering of the barrier, whereas splitting off of water from methanetriol is practically without any barrier, which explains the fact that formic acid does not exist in the hydrated form. The deprotonations of both formaldehyde and formic acid in gas phase are connected with high barriers, the barrier of formic acid being higher due to the stabilization effects of hydroxyl group on the positive charge. The barrier is fundamentally de-

creased by the influence of water in both of the two cases. It can be presumed that in a real medium (where the protonated molecule is surrounded by a cluster of water molecules) the barrier will be still lower.

The MINDO/3 method cannot describe the hydrogen bond between methanediol or methanetriol and a cluster of water molecules. However, it gives a stable associate of the protonated formaldehyde or protonated formic acid with water. The geometry of the molecules studied is described by the method relatively well. Under- or over-estimated are only those bond lengths and angles which are known to belong to the standard drawbacks of this method[20,21].

REFERENCES

1. Burnett M. G.: J. Chem. Educ. 59, 160 (1982).
2. Bell R. P., Evans P. G.: Proc. Roy. Soc., A 291, 297 (1966).
3. Gorrie T. M., Kalayna Raman S., Rouette H. K., Zollinger H.: Helv. Chim. Acta 56, 175 (1973).
4. Iliceto A.: Gazz. Chim. Ital. 84, 536 (1954).
5. Cordes E. H. in the book: The Chemistry of Carboxylic Acids and Esters (S. Patai, Ed.), p. 632. Interscience Publishers, London — New York — Sydney — Toronto 1969.
6. Williams I. H., Maggiora G. M., Schowen R. L.: J. Amer. Chem. Soc. 102, 7831 (1980).
7. Thang N. D., Hobza P., Pancíř J., Zahradník R.: This Journal 43, 1366 (1978).
8. Jeffrey G. A., Pople J. A., Radom L. A.: Carbohydrate Res. 25, 117 (1972).
9. Lathan W. A., Radom L., Hehre W. J., Pople J. A.: J. Amer. Chem. Soc. 95, 699 (1973).
10. Bingham R. C., Dewar M. J. S., Lo D. H.: J. Amer. Chem. Soc. 97, 1302 (1975).
11. Bingham R. C., Dewar M. J. S., Lo D. H.: J. Amer. Chem. Soc. 97, 1294 (1975).
12. Vishveshwara S.: Chem. Phys. Letters 59, 30 (1978).
13. Spelbos A., Mijlhaff F. C., Faber D. H.: J. Mol. Struct. 41, 47 (1977).
14. Pople J. A., Gordon M. S.: J. Amer. Chem. Soc. 89, 4253 (1967).
15. Sutton L. E.: Tables of Interatomic Distances and Configuration in Molecules and Ions. The Chemical Society, London 1958.
16. Lawrence R. B., Strandberg M. W. P.: Phys. Rev. 83, 363 (1951).
17. Wiliams D. H., Spangler D., Fence D. A., Maggiora G. M., Schowen R. L.: J. Amer. Chem. Soc. 102, 6619 (1980).
18. Klopman G., Andreozzi P., Hopfinger A. J., Kikuchi O., Dewar M. J. S.: J. Amer. Chem. Soc. 100, 6267 (1978).
19. Symons M. C. R.: J. Amer. Chem. Soc. 102, 3982 (1980).
20. Del Bene J. E.: J. Amer. Chem. Soc. 100, 1673 (1978).
21. Del Bene J. E., Radovick S.: J. Amer. Chem. Soc. 100, 6936 (1978).

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