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Density-Functional-Theory-Based Molecular Dynamics Study of 1,3,5-Trioxane and 1,3-Dioxolane Protolysis

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Abstract: We present a density-functional-theory-based molecular dynamics study of the protonation reaction of 1,3,5-trioxane and 1,3-dioxolane. The dynamics of the reaction is followed through variations in molecular conformations as well as in the chemical bonding. Insight is gained into some of the elementary processes and reaction mechanisms relevant to complex polymerization reactions of wide application and of interest in industrial chemistry.

I. Introduction

One of the most formidable goals of theoretical chemical physics is to provide a microscopic understanding of polymerization reactions, namely of their driving mechanisms and dynamics. While a full and sound approach requires a correct account of both intra- and intermolecular interactions (short as well as long-range), the first steps in this search consist of investigating the molecular elemental reactions believed to characterize crucial steps of the polymerization process. This implies not only mastering the chemistry of the relevant monomers, which are building units or appear as intermediate species, but also describing the dynamics of fundamental reactions, which involve either the breaking or forming of chemical bonds and the change of molecular conformations. *Ab initio* molecular dynamics (MD)[1] appears to be a suitable method to tackle such phenomena, because it allows simulation of dynamical processes and calculates the atomic forces in a quantum scheme, which consists of treating the electronic problem in density functional theory (DFT).[2] In this paper, we apply this method to the study of the protolysis of 1,3,5-trioxane and 1,3-dioxolane, which are elemental processes relevant to the synthesis of acetal resins.[3,4]

1,3,5-Trioxane is the ring trimer of formaldehyde. It has long been recognized to be a good substitute for formaldehyde itself in the synthesis of polyoxymethylene. For the trioxane polymerization, a few facts have been established experimentally, e.g., that the reaction is acid-catalyzed and that an induction period exists when no polymer is formed. One of the open issues, which one would like to understand for a better control of the polymerization itself, concerns the kind of reactions that take place during this induction period. The most widely accepted hypothesis is that the cationic initiator associates with oxygen and that formaldehyde is released after the ring opens. No confirmation of this exists, however, nor does one have a clue to how this actually occurs. Moreover, it cannot be ruled out that, instead, an isomer of the protonized 1,3,5-trioxane is stable and plays the role of the building unit in the polymerization process.

Table 1. Geometrical Characteristics of Formaldehyde

	this work	exp[a]	NL-SCF[b] (TZ+2P)	CCSD[c] (TZ+2P)	MP2[d] 6-31G*
R(C−O) (Å)	1.232	1.208	1.209	1.204	1.221
R(C−H) (Å)	1.112	1.116	1.120	1.098	1.104
α(H−C−H)	116.6	116.5	116.2	116.6	115.6

[a] Reference 14. [b] Reference 17. [c] Reference 18. [d] Reference 19.

Table 2. Geometrical Characteristics of 1,3,5-Trioxane

	this work	exp[a]		this work	exp[a]
R(C−O) (Å)	1.445	1.422	β(H−C−H)	111.5	
R(C−H) (Å)	1.10		γ(O−C−O)	111.4	112.2
α(C−O−C)	109.9	110.3			

[a] Reference 15.

Table 3. Geometrical Characteristics of 1,3-Dioxolane

	this work	exp[a]		this work	exp[a]
R(C−O) (Å)	1.450	1.423	α(C−C−O)	103.2	101.0
R(C(3,4)−H) (Å)	1.096	1.106	β(H−C(3,4)−H)	117.3	118.0
R(C−C) (Å)	1.554	1.542			

[a] Reference 16.

Table 4. Formaldehyde: Vibrational Frequencies (in cm^{-1})[e]

	this work	exp[a]	NL-SCF[b] (TZ+2P)	CCSD[c] (TZ+2P)	MP2[d] (6-31G*)
ω_1	1086	1191 [1167]	1146	1209	1194
ω_2	1199	1287 [1249]	1200	1294	1249
ω_3	1455	1563 [1500]	1454	1559	1567
ω_4	1692	1764 [1746]	1747	1802	1786
ω_5	2870	2944 [2783]	2775	2963	3019
ω_6	2940	3009 [2843]	2834	3038	3064

[a] Reference 20. [b] Reference 17. [c] Reference 18. [d] Reference 19. [e] As experimental reference, we report the harmonic frequencies obtained from the measured values (in brackets).

1,3-Dioxolane is a five-membered ring diether, which, in contrast to 1,3,5-trioxane, contains one carbon−carbon bond.

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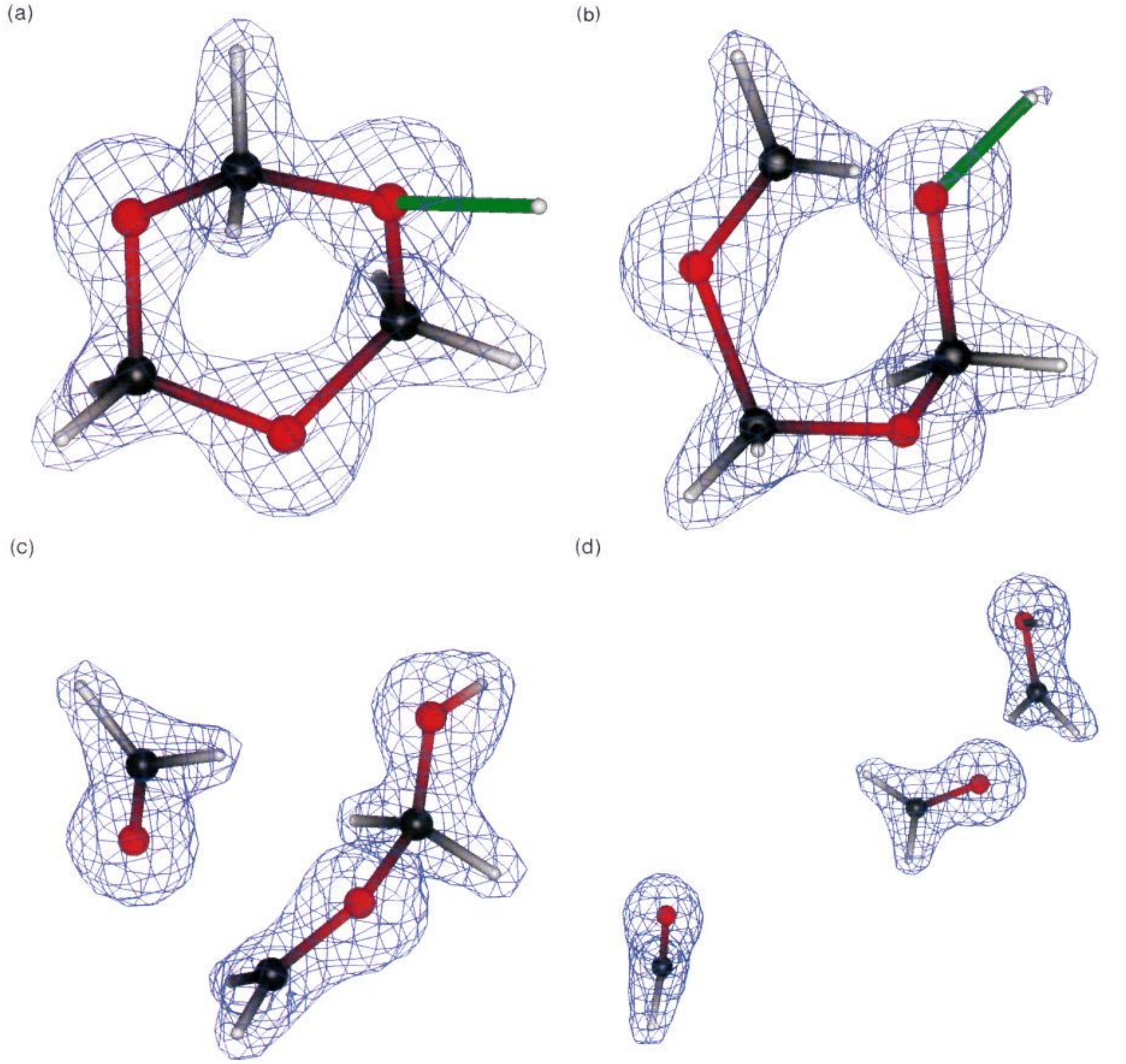

Figure 1. *Protonated 1,3,5-trioxane: instantaneous configurations of the simulation and the constant electron density surface of value 0.01 e/(au)^3* [(a) initial configuration, (b) ring-opening, (c) first dissociation, and (d) second dissociation]. (See text.)

Table 5. Formaldehyde: Dipole Moment DM (in Debye) and Proton Affinity PA (in eV)

	this work	exp	NL-SCF 6-31G*	QCSD 6-31G*	MP2 6-31G*
DM (D)	2.33	2.33[a]	2.022[b]	2.333[c]	2.275[d]
PA (eV)	7.70	7.58,[e] 7.45[f]			7.54[g]

[a] Reference 21. [b] Reference 22. [c] Reference 22. [d] Reference 22. [e] Reference 23. [f] Reference 24. [g] Reference 25.

Particularly together with 1,3,5-trioxane, it is used in copolymerization processes which give rise to a large variety of plastics with very interesting chemical and physical properties.[5] The question arises whether the two monomers exhibit different behavior after protonation and thus play a distinct role in copolymerization or not.

In order to gain some preliminary insight into these matters, we have investigated the protonation of 1,3,5-trioxane and 1,3-dioxolane, considered as isolated molecules. *Ab initio* DFT-based MD is in principle able to treat this type of reaction, as far as it can be considered adiabatic. After establishing the computational scheme, its input and accuracy, we shall present the results of the MD simulation and discuss the various steps of the reactions through the evolution of the gometrical conformations as well as through the transformation of their electronic configurations.

II. Computational Scheme and Molecular Equilibrium Structures

We apply the DFT-local density approximation (LDA)-based Car–Parrinello method, with gradient corrections to the exchange energy functional according to Becke's prescription (GCX–LDA).[6] This has been demonstrated to be critical for an accurate description of hydrogen-bonded systems,[7] so it will become of crucial importance at a more advanced stage of our simulations, where several interacting molecules will be considered and the propagation step of the polymerization process will be studied. In the isolated monomers, this gradient-

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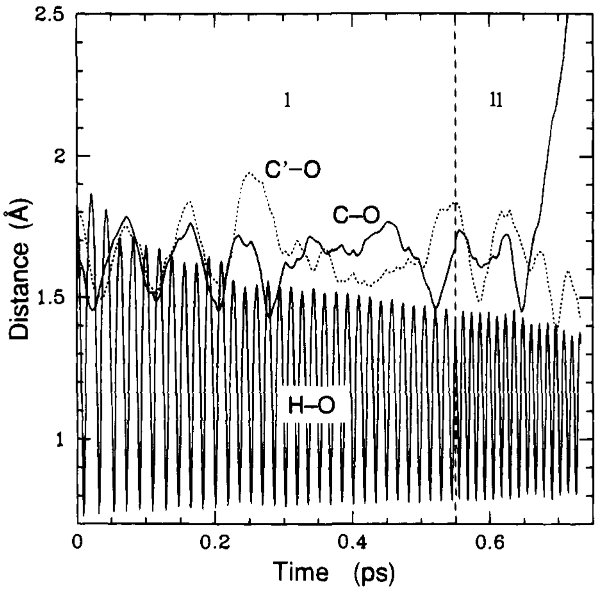

Figure 2. 1,3,5-Trioxane: temporal evolution of interatomic distances. C′ and C indicate the nonactive and the active carbon sites, respectively. Note that the plot starts 0.2 ps after the initial configuration of the simulation.

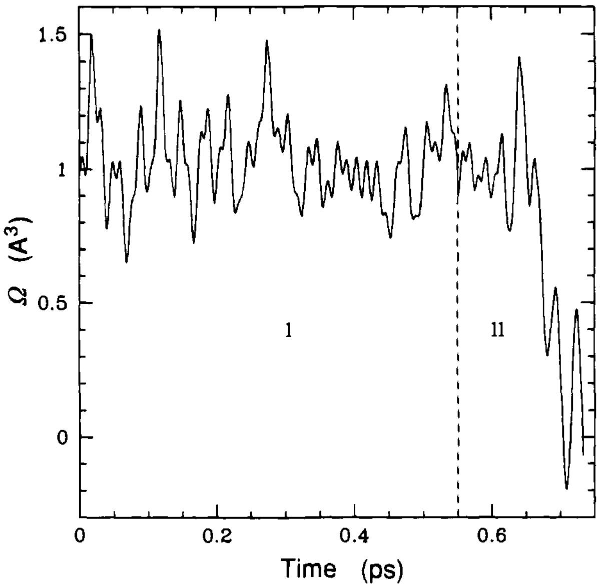

Figure 3. 1,3,5-Trioxane: vector product Ω of the three-bond vectors of the active carbon atom C as a function of time.

corrected local functional does not alter the geometrical characteristics obtained with LDA calculations but improves the values of the bond energies and the ability to describe dissociation processes.[8] The electronic wave functions are expanded in plane waves, and periodic boundary conditions (pbc) are used throughout the calculations. Convergence with respect to the cell size (face-centered-cubic with a 14.817 Å edge) has been checked in the case of 1,3,5-trioxane and for a few configurations against calculations made with a recently developed pbc-free scheme,[9] which is more suitable for free clusters. The atomic pseudopotentials, which are derived form all-electron GCX–LDA calculations, are of the Vanderbilt-type.[10] They have the advantage of providing results of reasonable accuracy in spite of a relatively low cutoff of their Fourier expansion. This is particularly true for oxygen. We have used an energy cutoff of 35 Ry. The characteristic radii of the Vanderbilt pseudopotentials are 1.2 au for C, 1.0 au for O, and 0.75 au for H.

Electronic and geometrical configurations were optimized using a variation of the direct inversion iterative subspace (DIIS) method.[11] In our constant-energy and constant-volume MD simulations, the coupled equations of motion for the electronic and ionic variables were integrated using the velocity-Verlet algorithm,[12] using a time step of 0.12 fs and an electronic effective mass of 500 au. The final part of the calculations was carried out with a more advanced technique which allows for larger time steps and is based on a more efficient integration scheme.[13] A simulation of 1 ps for the case of trioxane takes about 50 h on an IBM RISC-590. Tables 1–3 contain the geometrical characteristics of formaldehyde, 1,3,5-trioxane, and 1,3-dioxolane calculated with the above scheme. The reference experimental data are from microwave spectroscopy for formaldehyde[14] and 1,3,5-trioxane[15] and from electron-diffraction data for 1,3-dioxolane.[16] Comparison with sophisticated first-principle calculations is possible only for formaldehyde.[17–19] Convergence of our calculated values with respect to the energy cutoff was checked up to 70 Ry. The only noticeable discrepancy between our calculated values and the measured ones is the C–O bond length, which is overestimated by about 2%. This may be due to the use of a pseudopotential scheme. On the other hand, the agreement could probably be improved by introducing gradient corrections in the correlation energy functional as well. However, this is less accurate for the description of intermolecular interactions,[7] in which we are also interested.

A more stringent test of the computational scheme, which is also relevant to the present study, must be searched in the description of the dynamical and electronic properties as well as in the determination of the energetics involved in the protonation reaction. Again, an exhaustive comparison can be made only in the case of formaldehyde. Tables 4 and 5 report our calculated values for the vibrational frequencies (in the harmonic approximation), the dipole moment and the proton affinity of formaldehyde, and the comparison with both experimental data and results of first-principles calculations. This confirms the relatively high accuracy of our approach.

III. Simulation of the Protonation Reaction

In our constant-energy simulations of both 1,3,5-trioxane and 1,3-dioxolane, we have first equilibrated the molecule at about room temperature. Being small aggregates, temperature fluctuations of the molecules were relatively large (≈20%). At this temperature, the molecular geometry of the ground state is fully preserved. In the average room-temperature structure, the C–O and C–H bond lengths are expanded by less than 2%.

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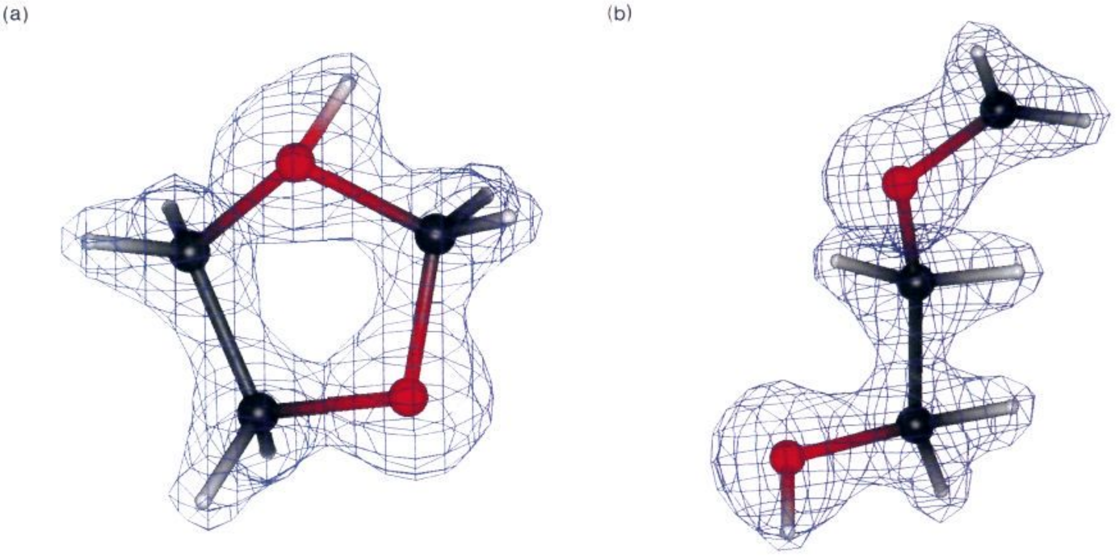

Figure 4. Protonated 1,3-dioxolane: instantaneous configurations of the simulation and constant electron density surface of value 0.01 e/(au)^3 [(a) initial configuration and (b) ring-opening].

We then added the proton such that the closest distance to an oxygen atom was as large as 1.5 Å. The initial configurations are shown in Figure 1a and 4a, where a constant electron density surface is also plotted to show the bonding pattern. We notice, in particular, the sp^3 hybridization on the carbon atoms and the weak polarization of the electron density on the oxygens. We thus let the systems evolve freely, and, following their temporal evolution, we observed drastically different behavior for the two molecules. In both cases, monitoring of the behavior of the electronic structure showed that the hypothesis of adiabaticity was verified.

(A) 1,3,5-Trioxane. The evolution of 1,3,5-trioxane can be divided into four major steps.

(i) During the first phase, which lasted about 0.7 ps, the proton approached the closest oxygen and executed an oscillatory motion of frequency ≈1790 cm^{-1}, adiabatically decoupled from the rest of the molecule. This motion is shown in Figure 2, where the H−O distance is plotted as a function of time. It was accompanied by an asynchronous modulation of the C−O bond lengths, as can also be seen in Figure 2. Noticeably, we observed a progressive charge transfer from the molecule to the proton.

(ii) As illustrated in Figure 2, the frequency increases rapidly and stabilized itself at 2760 cm^{-1}. This corresponds to the formation of an OH bond of average length ≈1.1 Å. These values can be compared to those typical of OH bonds in alcohols: $d(\mathrm{OH}) = 0.96$ Å and $\nu \approx 3100-3500$ cm^{-1}. After only another 0.15 ps, we observed the sudden breaking of one of the C−O bonds (Figure 2). The ring opened (Figure 1b), and a carbocation was formed. As a consequence, rehybridization took place at the level of the charged carbon atom from sp^3 to sp^2. We can quantify this process by measuring the volume Ω spanned by the three carbon bond vectors. We evaluate it with a triple vector product, thus arbitrarily assigning a sign to the volume. The latter allows us to monitor the atomic oscillations through the sp^2 plane. As a geometrical visualization of this process, Figure 3 shows the time variation of the vector product of the three carbon bond vectors. We see that, coincidental with the breaking of the C−O bond in Figure 2, this value drops suddenly to zero. The process of forming the OH bond and breaking a C−O bond is mirrored in the behavior of the one-electron (Kohn−Sham) energy levels. In the initial configuration, the presence of a proton creates a diffuse state in the HOMO−LUMO gap of the molecule. After proton attachment and ring opening, the formation of the OH bond is signaled by the existence of an occupied state about 1 eV below the HOMO level. Ring-opening also corresponds to the opening of a large HOMO−LUMO gap (≃4 eV in LDA).

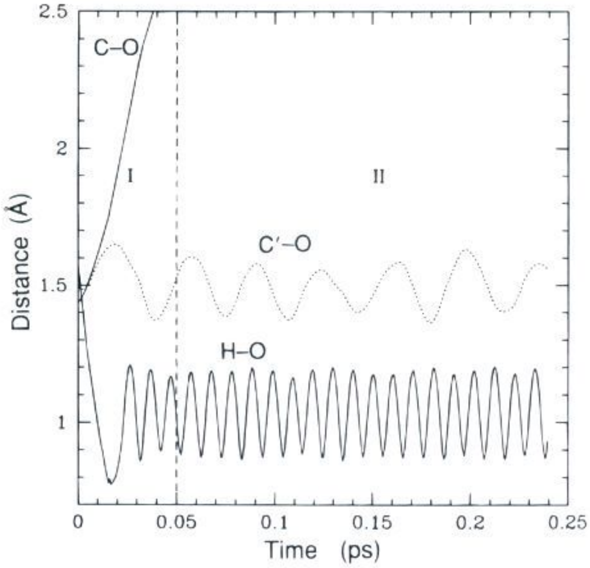

Figure 5. 1,3-Dioxolane: temporal evolution of interatomic distances. Notations as in Figure 2.

(iii) The open-ring protonated trioxane molecule was clearly unstable. After only 0.1 ps, it expelled one formaldehyde molecule, thus generating a new carbocationic intermediate (Figure 1c).

(iv) The lifetime of the $^+\mathrm{CH_2OCH_2OH}$ intermediate was very short. After about 0.2 ps, it dissociated into one neutral and one protonated formaldehyde molecule (Figure 1d).

We followed the system of the three separated molecules for ≈1 ps and did not observe any further significant change, i.e., no tendency either to undergo associations or dissociations. The system spontaneously equilibrated at a temperature of ≈650 K.

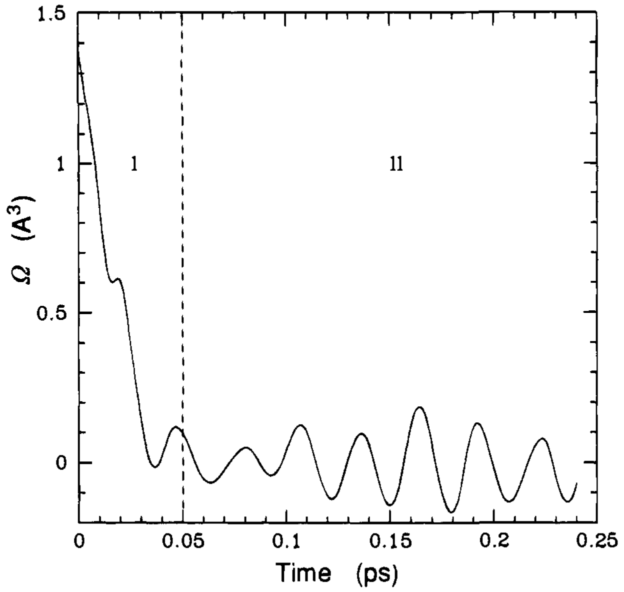

Figure 6. 1,3-Dioxolane: vector product of the three-bond vectors of the active carbon atom C as a function of time.

The above results can thus be expressed by the chemical formula

$$\underline{CH_2OCH_2OCH_2O} + H^+ \rightarrow \underline{CH_2OCH_2OCH_2OH}^+ \rightarrow$$
$$^+CH_2OCH_2OCH_2OH \rightarrow CH_2O + {}^+CH_2OCH_2OH \rightarrow$$
$$2CH_2O + {}^+CH_2OH$$

Clearly, the time interval necessary for the proton attack of the trioxane will depend on the initial conditions of the simulation. Being that the attack is not instantaneous, however, it will cause the proton to lose memory of the initial configuration. Thus, we believe that this does not affect the final result. Comparison with experiment is not possible at this stage. However, the present study shows that, at least in the case of an isolated molecule, the protonated ring isomer is metastable and that, once the ring opens, the dissociation into formaldehyde units follows very rapidly.

(B) 1,3-Dioxolane. In this case, the protonation reaction is reduced to only two steps.

(i) After less than 0.05 ps, a strong OH bond is formed and the five-membered ring opens (Figure 4b) corresponding to the carbon atom bridging the two oxygens. This is clearly illustrated in Figures 5 and 6. In fact, Figure 5 shows that the oscillations of the O–H distance quickly stabilize at ≈3150 cm^{-1}, i.e., around the typical frequency of the OH stretching, and that one CO bond breaks while the other one remains insensitive to the reaction. In Figure 6, the volume spanned by the three carbon bonds signals again the sudden transformation from sp^3 to sp^2 hybridization, which accompanies the ionization of the carbon atom.

(ii) During the rest of the simulation, which we followed for another ≈3.5 ps, the linear carbocationic monomer (Figure 4b) stabilized at an average temperature of ≈750 K, and no loss of formaldehyde molecules was observed. The monomer was rather floppy, due to soft torsional forces.

In conclusion, the protolysis of 1,3-dioxolane results in the formation of a linear carbocationic monomer, which appears to be stable against dissociation. The fact that the ring opens at the carbon bridging the two oxygens, instead of at one of the two bonded carbons, is a nontrivial result. Selection of the route could well depend on the initial conditions of the simulation. However, it must be emphasized that the atomic arrangement we find for the linear isomer is indeed the one which has a higher probability of dissociation with the release of a formaldehyde molecule. As no dissociation is observed, which is the most relevant result of our calculations, we tentatively conclude that our result is not biased by the initial conditions. However, it must be added that dissociation might occur on a time scale longer than that of our simulation.

IV. Discussion and Conclusions

Based on our results for the protonation reaction of the isolated monomers of 1,3,5-trioxane and 1,3-dioxolane, a few facts can be established, which help us understand some experimental observations for the more complex systems.

The simulation of trioxane shows that hydrogen attachment is not immediate and proceeds through a series of complicated steps. This might be one of the possible reasons for the observed induction period in the trioxane polymerization, during which no polymer forms. Such an induction period does not exist in the case of pure formaldehyde polymerization. We have performed simulations of the protonation of pure formaldehyde in the solid as well as in the liquid phases at room temperature, using a model of 18 molecules per unit cell. Indeed, we have observed in this case the immediate triggering of the polymerization reaction.

Our study shows that the behavior of 1,3,5-trioxane is dramatically different from that of 1,3-dioxolane. First, the ring opening was immediate in the latter and required about 700 fs in the former. Second, only in the case of 1,3,5-trioxane was it followed by the (rapid) release of formaldehyde units. These findings are consistent with the experimental observation of almost exclusively dioxolane monomeric units[26] as the growing chains in the initial stage of 1,3,5-trioxane-1,3-dioxolane copolymerization.

The *ab initio* treatment of the molecular systems as well as simulations of the dynamics of the reactions are crucial for the correct description of the evolution of molecular systems for unraveling their microscopic mechanisms. Car–Parrinello simulations carried out for a system with several molecules are necessary to provide a more realistic model and to enable us to investigate the polymerization process. Such calculations are now underway.

V. Acknowledgments

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