

Thermal decomposition of gallium nitrate hydrate and modeling of thermolysis products

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Abstract It is well established that gallium insertion into the hydroxiapatite matrix as practiced in orthopedics protects bone from resorption and improves the biomechanical properties of the skeletal system. The research presented in this article is an investigation into the thermal decomposition of gallium nitrate, which is part of a complex process leading to the preparation of a hybrid matrix. It was demonstrated that after melting of the hexahydrate in its own water there occurs a simultaneous condensation of 4 mol of initial monomer $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ into a tetramer $\text{Ga}_4\text{O}_4(\text{NO}_3)_4$. The resulting inorganic cycle gradually loses N_2O_5 and, through the formation of unstable oxynitrates, is transformed into gallium oxide. The use of molecular mechanics for comparing the potential energies of consecutive products of thermal decomposition permitted an evaluation of their stability and an appropriate interpretation of the experimental data.

Keywords Gallium nitrate hexahydrate · Thermal decomposition · Computer modeling

Introduction

Gallium most commonly enhances the calcium and phosphorus content of bone and has direct noncytotoxic effects on osteoclasts at markedly low doses [1]. Its future usage,

in the form of gallium nitrate, will provide an opportunity to prepare biomaterials for the stimulation of bone growth and calcium retention. We had already obtained gallium-doped hydroxyapatite for orthopedic purposes by employing $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ as the gallium source [2]. This result, we believe, supports the need for and value of further investigation, such as that presented in this paper. Greater knowledge of the mechanisms involved in the thermal behavior of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ may improve our understanding of synthetic strategies and the design of multifunctional biomaterials.

The thermal decomposition of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ has also been the subject of recent research using thermal analysis techniques, differential thermal analysis (DTG), and differential scanning calorimetry (DSC) performed at a number of different heating rates [3]. Although the general conclusions of this research work are unobjectionable, it is possible, in our opinion, that a simpler and more convincing mechanism of thermal decomposition than that proposed by the authors may be found. In particular, it seems doubtful that gallium hydroxide could be considered as an intermediate product of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ disintegration. The purpose of our own research is to revert to the thermolysis of the above hydrate $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, offering a different and more realistic scheme of events. Besides thermal analysis we have used the molecular mechanics method in order to build up the structural models, calculate their minimal potential energy and, on this basis, compare the stability of what we regard as the true intermediates.

Experimental

The starting reagent used in our experiments was gallium nitrate hydrate $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ of analytical grade purity

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purchased from Sigma-Aldrich. Thermal gravimetric analysis and differential scanning calorimetry were used to study thermal behavior, in both cases employing 50H Shimadzu Instrumentation. Test specimens of the starting material were heated in a flux of nitrogen at heating rates 3, 5, and 10 °C min⁻¹. Mass losses during heating were analyzed and compared to previously calculated values. Melting point was determined using the standard capillary method.

Compounds were simulated using the standard GHEMICAL 2.98 software package. All models were submitted to a rigorous conformational analysis by implementation of the Tripos 5.2 force field program [4]. Geometries were found by minimizing the energy with respect to all geometrical variables, no assumptions being made other than that of appropriate symmetry. Bond angles and interatomic distances were evaluated by using special features of the program. In the literature at our disposal, we have been unable to find any theoretical foundations for the construction of primary models of gallium compounds.

We are fully aware that the simulation of the structure of solid compounds by the molecular mechanics method can sometimes lead to very dubious results. Nevertheless, some understanding of such aspects as the degree of stress of closed cycles, the comparative size of functional groups, possibilities of rotation, and so on may prove useful for our general understanding of the structure of real compounds and our ability to assess their stability.

Results and discussion

Our experiments have shown that direct heating of the commercial reagent Ga(NO₃)₃·xH₂O produces a mass loss of 75.1%, which corresponds to $x = 6$. This is a reasonable figure, as nitrates of the cations with charge 3+, e.g., Al, Sc, Y, and lanthanides, are usually characterized by the number of water molecules, ranging from 4 to 9H₂O [5–7]. The existence of hexaaquagallium ion [Ga(OH₂)₆]³⁺ was positively confirmed, at least in water solutions [8]. In our opinion, there is no reason to believe that the mechanism of Ga(NO₃)₃·6H₂O thermal decomposition might differ from that of octahydrate, which was studied in the work cited earlier [3]. We agree with its authors that the heating rate considerably affects the composition of intermediate compounds. In our own research, the most detailed TG curves were obtained for a heating rate of 5 °C min⁻¹. In order, therefore, to obtain representative results, we chose this velocity as our basic run performance.

As established by visual observations, the compound becomes liquid at around 50 °C. The TG and DSC curves of Ga(NO₃)₃·6H₂O are illustrated in Figs. 1 and 2. It is well known that the decomposition onset for the nitrates of

transition metals is generally below 100 °C due to a back-donation of electrons from the nitrate ions to an unfilled *d*-orbital of the cations [9]. In this respect, gallium nitrate is not an exception. According to the TG curve, it melts in its own water of crystallization at 44 °C losing 7.40% of mass. The largest loss of mass (36.55%) takes place between 77 and 118 °C. There rapidly follow two losses of 11.50 and 5.04% at 134 and 146 °C, respectively. The last considerable loss of mass (7.38%) occurs at 194 °C. The remaining mass diminishes slowly and gradually, becoming constant at 400 °C.

The DSC curve (Fig. 2) confirms melting point at 43.9 °C and the removal of volatile components at higher temperatures, but it is completely unsuitable for calculations, since small endothermic effects are practically imperceptible.

It is obvious that the loss of mass which takes place during the first two stages, a total of 43.95%, cannot possibly result from the disintegration of the single mol of Ga(NO₃)₃·6H₂O, if only because it contains no more than

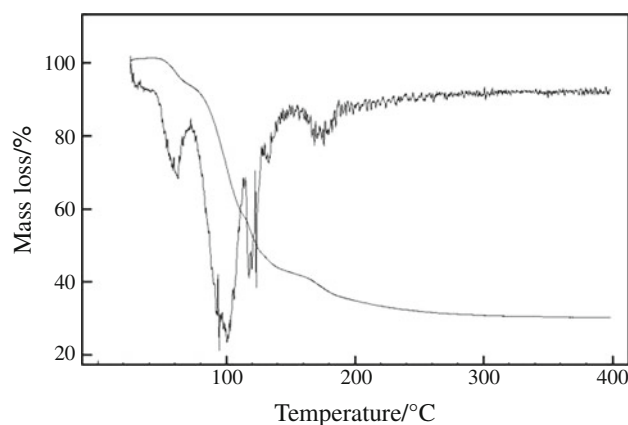


Fig. 1 TG curve of 4[Ga(NO₃)₃·6H₂O]

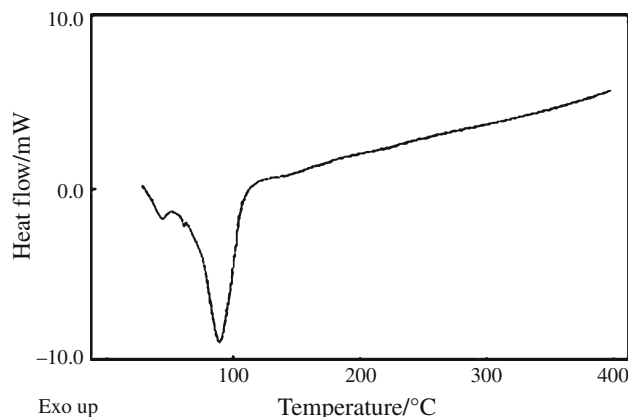


Fig. 2 DSC curve of 4[Ga(NO₃)₃·6H₂O]

one atom of metal, whereas at least two are required for the formation of Ga_2O_3 . Consequently, we must take into consideration the process of condensation, characteristic of the chemistry of cations with the charge +3. Here, it is worth referring to the existing published data on the elements whose properties are close to gallium. For scandium, for example, it has been shown that such condensation leads to the formation of stable groups containing four metal atoms [7]. As to gallium itself, cyclic clusters containing four gallium atoms, $\text{Ga}_4(\text{OH})_4(\text{CH}_3)_8$ and $\text{Ga}_4\text{O}_6(\text{OH})_x$ have been isolated in solid form [10, 11].

Calculations show that the hypothesis concerning cluster pre-existence in the solid state is quite applicable to the present case of gallium nitrate hydrate. Indeed, that suggests that in the condensation process at least 4 mol of $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ are involved, and the total decomposition can be described as



This gives a total mass loss of volatile products of 74.2%, which corresponds well to the experimental value of 75.1% obtained after treating gallium nitrate at 800 °C for 2 h. Naturally, we might start considering the condensation of $2[\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$, as in the case of gadolinium sulfate octahydrate [12] but in this case, at the end of the process, we would have to resort to fractional values of stoichiometric coefficients for N_2O_5 .

Another possibility is that the tetrameric clusters precede thermal treatment, and that $6\text{H}_2\text{O}$ stabilize them through a system of hydrogen bonds. In any case, it does not affect the interpretation of DTG results.

As for the individual stages of thermal decomposition, the DTG curve can be explained as follows.

At the first stage, during the process of the initial melting of the compound and immediately afterward 6 mol of loosely bound water are removed. This produces a mass loss of: calc. 7.42%; exper. 7.40%. Up to this point, there has been no interaction between individual molecules of $\text{Ga}(\text{NO}_3)_3$, although the stability of clusters may have decreased.

At the second stage, $5\text{H}_2\text{O}$ and $4\text{N}_2\text{O}_5$ are removed, producing a mass loss of: calc. 35.8%; exper. 36.55%. The removal of $4\text{N}_2\text{O}_5$ leads to the creation of oxygen bridges between the gallium atoms, obliging $4\text{Ga}(\text{NO}_3)_3$ to condense into a tetrameric structure as demonstrated in the following scheme:

At the third stage, $9\text{H}_2\text{O}$ are removed, producing a mass loss of: calc. 11.13%; exper. 11.50%. At the fourth stage, the remaining water is eliminated. This gives us a mass loss of: calc. 4.94%, exper. 5.04%. After complete dehydration, at the fifth stage, the penultimate molecule of N_2O_5 is lost. In this case, the mass loss is: calc. 7.40%, exper. 7.38%.

Finally, the last N_2O_5 is removed (calc. 7.4%; exper. 7.33%) and there are no further thermal transformations. At this stage, the oxygen-containing bridges are unable to withstand the strain and collapse, leaving behind 2 mol of Ga_2O_3 . In total, the partial losses comprise 74.29, which is close to the 75.1% reached by heating directly to 800 °C.

The models obtained by using the molecular mechanics technique are shown in Figs. 3 and 4. As can be seen in Fig. 4, the base of the tetramer is formed by an inorganic heterocycle composed of four atoms of gallium, alternating with four atoms of oxygen, which, to simplify things, are numbered from 1 to 8. The gallium and oxygen sub-units are located in different planes. According to our calculations, the interatomic distances between gallium and oxygen are as follows: $\text{Ga}(2)\text{--O}(3)$ 1.11 Å, $\text{Ga}(4)\text{--O}(5)$ 1.15 Å, $\text{Ga}(6)\text{--O}(7)$ 1.09 Å, and $\text{Ga}(8)\text{--O}(1)$ 1.10 Å. The bond angles Ga--O--Ga are also non-equivalent: $\text{Ga}(2)\text{--O--Ga}(4)$ 112.30°; $\text{Ga}(4)\text{--O--Ga}(6)$ 113.13°, and $\text{Ga}(6)\text{--O--Ga}(8)$ 110.27°. It is interesting to note that the values of the bond angles are very close to those of $\beta\text{-Ga}_2\text{O}_3$ [13], which is the only stable modification. These bond angles were determined by the X-ray technique, using a single crystal of gallium oxide [14].

Since the bonds Ga--O forming the cycles are not covalent, but rather ionic in nature, it becomes quite clear that, in contrast to the planar benzene ring, these cycles can easily become corrugated. Moreover, as the angle of this "folding" may vary within certain limits, one can expect to

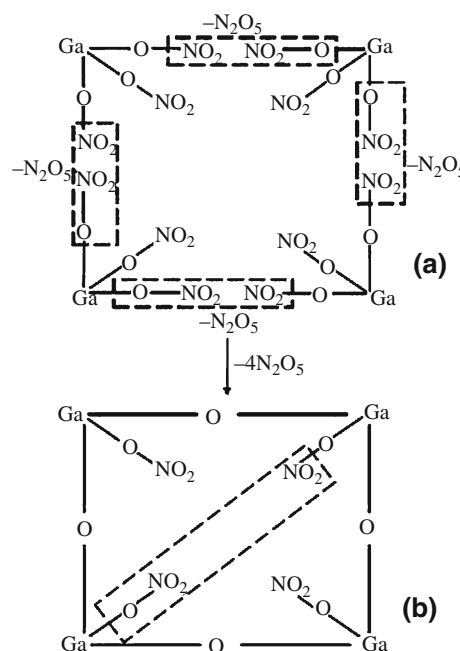


Fig. 3 Scheme showing the condensation process of $4[\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$. **a** Initial monomers; **b** final unstable tetramer

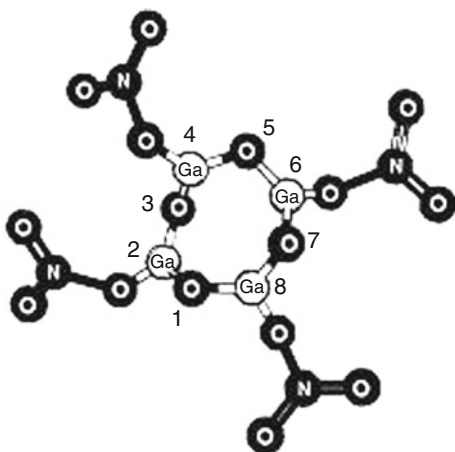


Fig. 4 Model of tetramer structure containing 4NO_3^-

find the presence of conformational isomers with slightly differing values of potential energy. In a real solid, this degree of freedom is unlikely to be preserved due to the requirements imposed by the densest packing. The same is true of the degree of freedom of rotation about the bonds between gallium and oxygen of NO_3^- groups in the positions 2, 4, 6, and 8 of the cycle. These groups behave as normal nitrate anions with N–O distances in the range 1.10–1.14 Å, that is slightly shorter than the bond lengths in the NO_3^- groups of solid nitrates established by X-ray methods (1.20–1.22 Å) [9]. Meanwhile, the bond angles O–N–O found for the model are equal to the angles in solid nitrates (close to 120.0°) in accordance with the actual structure of the polyatomic ion which has trigonal planar geometry.

There is one further point to consider in connection with the anions NO_3^- . As the model is based on the real relationship of the ionic radii, it is reasonable to assume that under no circumstances can relatively large anions be located inside the cycle which can be seen in simplified form in Fig. 5a. This inner space is too small to accommodate even a single anion, so the anions are “looking” outward, some anterior to the plane of the sheet, others posterior. For this reason, further condensation with removal of the distant NO_2 groups becomes difficult to achieve; hence the slow kinetics.

Unfortunately, we know too little about the localization of water molecules retained at high temperatures. Judging by their fractional and difficult removal, they seem to be coordinated directly by gallium atoms. Because of the strength of the bonds with oxygen, the loss of N_2O_5 , even at moderate temperatures, is the energetically more profitable process rather than the loss of closely coordinated water.

Figure 5a shows the structure that might be formed after the removal of the penultimate mol of N_2O_5 . Here, the

numeration of the cycle is the same as for the previous model. In this instance, the cross-bridge Ga–O–Ga connects positions 2 and 6. In view of the exceptional narrowness of this space (the distances between Ga(2) and Ga(6) are about 1.71 Å), the oxygen atoms are located far outside the cycle. The “legs” of the bridge are at a bond angle of 101.73° in relationship to each other, which is lower than the angles Ga–O–Ga within the cycle, where there is an average of 110.60° . The profile projection given in Fig. 5b shows that the cycle has become more bent in relation to the newly established bonds. At the same time, the remaining anions have attached themselves to gallium atoms situated at the back of the system, in positions 4 and 8. This is a clear indication of the instability of the entire structure, which could only have been formed as a metastable phase.

One would expect the final loss of N_2O_5 to produce another bridge, this time in a perpendicular direction. However, the strain increases to such an extent that the entire structure collapses, and 2 mol of gallium oxide are formed from its fragments.

The calculation of minimal potential energies for the aforementioned models shows that their numerical values for both tetramers, $\text{Ga}_4\text{O}_9(\text{NO}_2)_6$ and $\text{Ga}_4\text{O}_8(\text{NO}_2)_4$, are, in an arbitrary scale, very low, i.e., -131.3 and -73.1 kJ/mol. That means that the corresponding compounds may be formed easily and possess a certain stability. On the other hand, for the structure with an oxygen bridge across the

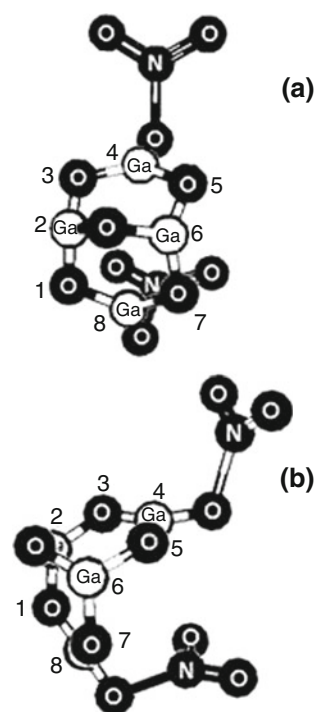


Fig. 5 Model of tetramer structure containing 2NO_3^- . **a** Front view of the cycle; **b** profile view of the cycle

cycle, connecting Ga(2) and Ga(6), as shown in Fig. 5, a big leap in potential energy from negative values to 20.9 kJ/mol is observed. This is a clear indication that this structure is comparatively unstable. The exceptionally high level of potential energy for a hypothetical Ga_4O_6 (177.0 kJ/mol) shows that the existence of a second bridge is practically impossible. As to the final Ga_2O_3 , its potential energy, as expected, is reasonably low, that is -0.4 kJ/mol.

It is clear that the levels of potential energy, calculated by means of molecular mechanics do not necessarily have any physical meaning in themselves. However, when considering a series of related structures, the method is extremely useful since (along with X-ray diffraction) it can reliably predict the differences in stability between one compound and another and be of help when interpreting the experimental findings of thermal analysis.

Conclusions

1. The thermal decomposition of gallium nitrate is a complex process, which begins with the simultaneous condensation of 4 mol of the initial monomer $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.
2. The resulting cyclic tetramer $\text{Ga}_4\text{O}_4(\text{NO}_3)_4$ gradually loses N_2O_5 and, through the formation of unstable oxynitrates, is transformed into gallium oxide.
3. The molecular mechanics method used for comparison of the potential energies of consecutive products of thermal decomposition permits an evaluation of their stability and a proper interpretation of experimental data.
4. The models of intermediate oxynitrates represent a reasonably good approximation to the real structures.

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