Investigation of Deuterated FOX-7 – Changes in Structural Behavior and Energetic Characteristics after Deuteration at ambient conditions

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Investigation of Deuterated FOX-7 – Changes in Structural Behavior and Energetic Characteristics after Deuteration at ambient conditions

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For an investigation of the deuterium effect on *N*-deuterated compounds on the structural and thermal behavior, 1,1-diamino-2,2-dinitroethylene (FOX-7) was deuterated by deprotonation in heavy water and subsequent acidification with D_2SO_4. The status of deuteration progress was monitored by infrared spectra analysis and the deuteration level determined via ^{1}H q-NMR. The properties of FOX-7-D_4 were studied by single crystal X-ray diffraction and differential thermal analysis. In addition, the activation energy of thermal decomposition was determined, and the heat of formation and zero-point energy were calculated.

In the past, various energetic materials have been isotopically modified with deuterium, some of which are shown in Figure 1. The main reason for deuteration was to investigate their different physical and chemical properties compared to the "normal" hydrogenated homologues. Interestingly, in all of the examples shown in Figure 1, only C-H bonds were deuterated.

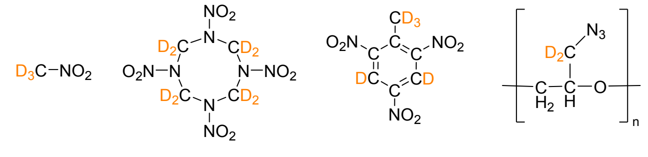

Figure 1. Molecular structures of deuterated energetic materials, which have been reported previously in the literature.[1–4]

The previously reported examples not only classical secondary explosives such as HMX[1] (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and TNT[2] (2,4,6-trinitrotoluene), but also propellant ingredients as nitromethane[3] as well as the energetic polymer GAP[4] (glycidyl azide polymer). In the research of energetic materials, the decomposition process has one of the most important roles and therefore it is important to elucidate the mechanism which occurs. For example, by understanding which decomposition products are formed and in which composition, allows knowledge about the long-term stability, explosion performance and sensitivity of the compounds. For such investigations, it is necessary for the hydrogenated compound to be compared with the deuterated one. For example, Kaiser *et al.* studied nitromethane and nitromethane-d_3 as the simplest model and example of energetic nitro-*CDNO*-compounds.[3]

However, the deuteration of energetic materials not only allows a better understanding of their decomposition mechanism, but also shows the influence of the deuterium effect on the structure and thermal stability. This deuterium effect, or kinetic isotope effect in general, is observed when bonds to isotopes are built or broken, as the case in the thermal decomposition process of explosives.[5] This effect is particularly significant for cases in which exchange of hydrogen by deuterium occurs, since the mass of the atom is directly doubled by the isotope exchange involving H and D. The primary kinetic isotope effect states that bonds with deuterium have a significantly lower zero-point energy but at the same time a significantly higher activation energy than the same bond with hydrogen, because a C-H (D^0_{298}: 338.4 kJ mol^{-1}) bond breaks several times faster than a C-D (D^0_{298}: 341.4 kJ mol^{-1}) bond.[5] For energetic materials, this would mean that an energetic compound should show an increase in its energetic properties by a simple H/D exchange.

In this work, for the first time the influence of deuteration on the structural properties and the energetic characteristics of nitrogen-deuterium bonds was investigated using the well-known energetic compound FOX-7 (1,1-diamino-2,2-dinitroethylene) as an example.

For the synthesis of deuterated FOX-7, its acid-base equilibrium known from literature was exploited.[6] For this purpose, sodium deuteroxide solution was first prepared by dissolving elemental sodium in heavy water. FOX-7 was then dissolved in this solution and deprotonated *in situ* to give its conjugate base. After addition of concentrated deuterated sulfuric acid, the equilibrium was shifted again and the compound could be deuterated.[7]

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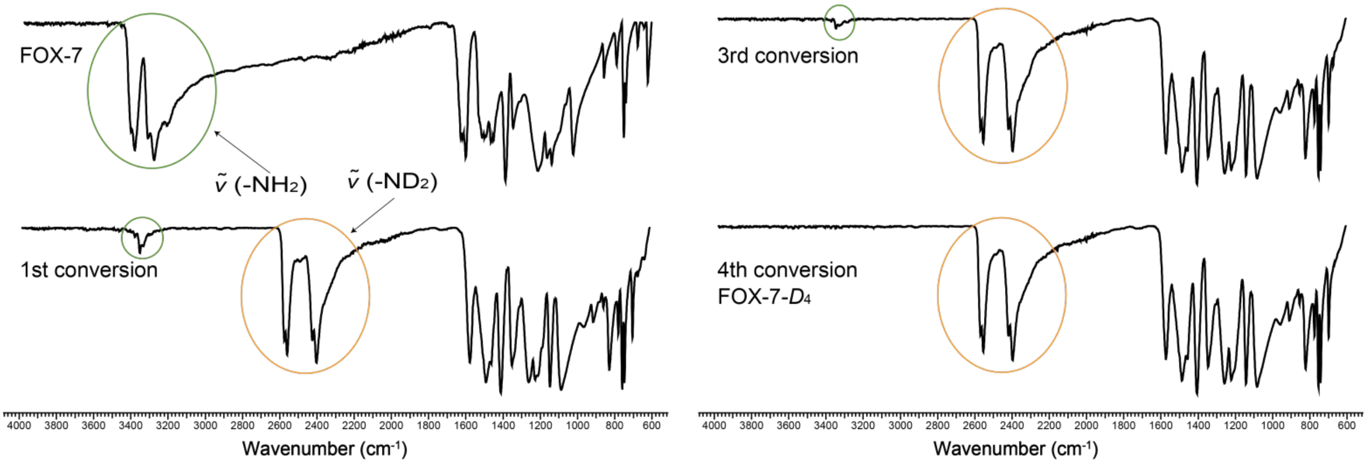
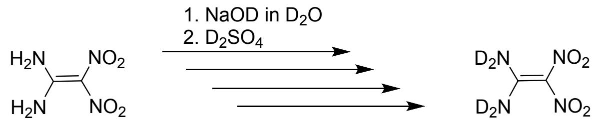


Figure 2. Infrared spectra of the different conversion steps from FOX-7 into FOX-7-D_4.

As indicated in Scheme 1, this synthesis was iteratively repeated four times in order to obtain the deuteration level as high as possible.

Since the amount of deuterated FOX-7-D_4 is exponentially increasing with each repetition and therefore only little amount of FOX-7 is left for deuteration, the process needed to be repeated only four times.



Scheme 1. Repeated (4 times) synthesis for the preparation of FOX-7-D_4.

The successful isotope labeling can be followed particularly well using IR spectroscopy, shown in Figure 2 with the different conversion steps.

The replacement of an atom by a heavier isotope leads to a downshift in wavenumbers.[8] In the IR spectra this red shift of the -NH_2 vibrations at 3500–3200 cm^{-1} to the -ND_2 vibrations at 2600–2200 cm^{-1} is clearly visible. Moreover, using IR spectroscopy the conversion was monitored, the -NH_2 peaks decrease with each repetition, while the -ND_2 peaks increase.

A comparison of the NMR spectra in DMSO-D_6 of FOX-7-D_4 with those of FOX-7 reveals only minimal differences. In the ^{14}N NMR spectrum only the resonance of the nitro group is visible for both at −25 ppm with no effect on NH or ND. In the ^{13}C NMR spectrum only a very small difference is detected for the amino bound carbon resonance (158.1 to 158.0 ppm for FOX-7-D_4). The carbon bound to the nitro groups remains at the same position for both isotopomers at 128.0 ppm. The deuterium resonance in the ^2D NMR spectrum (in DMSO-H_6) is detected as broadened singlet at 8.6 ppm.

For a determination of the exact isotopic purity, a quantitative ^1H NMR (q-NMR) was recorded using ethylene carbonate as external standard. According to equation for calculation of q-NMR,[9] the isotopic purity of FOX-7-D_4 is 95.7%.

It was possible to obtain single crystals of the deuterated species of FOX-7 (CCDC 2150220) by slow crystallization. FOX-7-D_4 crystallizes in the orthorhombic space group $Pna2_1$ as pale yellow blocks. This is somewhat surprising, in general it was expected that crystallization in the same space group as FOX-7 occur. Since hydrogen and deuterium do not differ in their electronic properties but only in the mass of the nucleus, FOX-7 and FOX-7-D_4 are by definition isosteric (same atomic number, electron number and atomic shells).[10] FOX-7, however, crystallizes in the monoclinic space group $P2_1/n$ published in 1998.[11] The density of FOX-7-D_4 recalculated to room temperature is 1.902 g cm^{-3}, which is as expected slightly higher than that of FOX-7 with 1.872 g cm^{-3} at room temperature, the recalculation method of the densities is explained in more detail in the Supporting Information (SI). The crystal structures of FOX-7 and FOX-7-D_4, as well as the corresponding Newman projections along the C=C axis and a section of their crystal package are shown in Figure 3. If the molecular structures of the two FOX-7 derivatives are compared, it can be concluded that the structure of the individual molecules do not significantly differ. The Newman projection highlights, that the -NH_2 and the -ND_2 groups are located in the C=C plane. In addition, in both compounds one of the two nitro groups almost lies in this plane, whereas the second nitro group is clearly twisted out of this plane. Comparing the dihedral angels of both compounds, the nitro groups in FOX-7-D_4 are slightly more twisted out the plane than in the non-deuterated FOX-7. A view at the two different crystal packings shows for both ABA zig-zag layers. However, after close examination, those of FOX-7 appear to lie identically parallel on top of each other with only a slight twist in the y axis. The layers of FOX-7-D_4, on the other hand, differ more clearly. The B layers are rotated and shifted by 180 degrees to the A layers. This could possibly be the reason that FOX-7-D_4 crystallizes in a different space group.

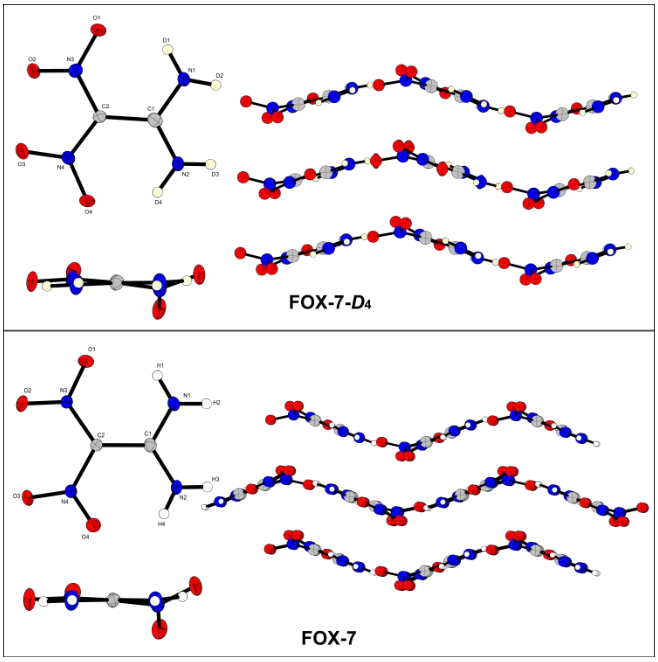


Figure 3. Top: Molecular structure, Newman projection and crystal package of FOX-7-D_4; Bottom: Molecular structure, Newman projection and crystal package of FOX-7[11]; Thermal ellipsoids of non-hydrogen atoms in all structures are set to the 50% probability level. Selected dihedral angels of FOX-7-D_4 (°): O4–N4–C2–N3 168.7(3), O3–N4–C2–C1 168.7(3), O1–N3–C2–N4 154.6(3), O2–N3–C2–C1 148.7(4). Selected dihedral angels of FOX-7 (°): N3–C2–N4–O4 −171.78(15), C1–C2–N4–O3 −171.03(15), N4–C2–N3–O1 −148.00(15), C1–C2–N3–O2 −143.57(16).

The experimentally determined (X-ray) solid state structures of FOX-7 and FOX-7-D_4 show one slightly shorter and one longer C-NO_2 bond, as well as one shorter and one longer C-NH_2/C-ND_2 bond. Both structures with their bond lengths are shown in Figure 4.

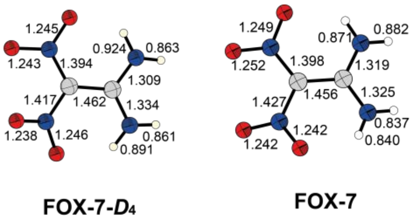


Figure 4. Molecular structures of FOX-7-D_4 and FOX-7[11] with their bond lengths.

The thermal behavior of FOX-7 has been extensively studied in the past. For example, two high-temperature modifications beta and gamma FOX-7 have been discovered.[6] The phase transition from alpha to beta can be observed at ca. 115°C, whereas the transition from beta to gamma occurs at ca. 173°C and decomposition being observed at about 228°C. By comparison of the DTA spectra of FOX-7 and FOX-7-D_4, Figure 5 shows that the deuterated compound has a decomposition temperature of 255°C, which is about 30°C higher than that of the non-deuterated compound.

As mentioned before, hydrogen bonds require less energy to be cleaved compared to deuterium bonds, which explains the higher thermal stability. The deuterated species also shows an endothermic signal at 114°C, which suggests a phase transition also for FOX-7-D_4 to another polymorph (which was not yet further investigated).

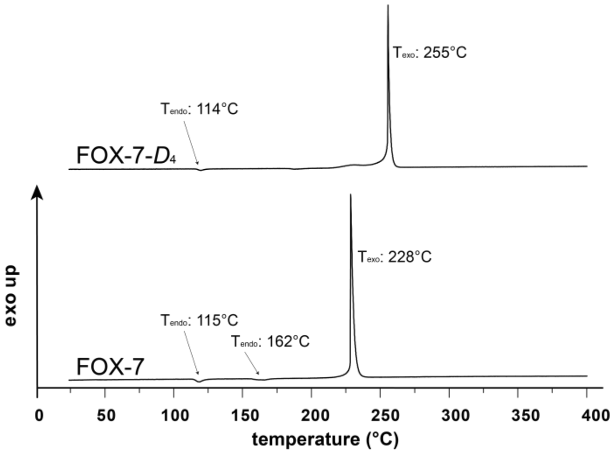


Figure 5. Differential thermal analysis spectra of FOX-7-$D_{4,}$ and FOX-7 with their onset temperatures measured in the range from 25°C to 400°C with a heating rate of 5°C min^{-1}.

The activation energy of the thermal decomposition as function of the conversion of FOX-7 and FOX-7-D_4 was determined using the NETZSCH Kinetics Neo software,[13] therefore thermal gravimetric analysis (TGA) measurements were performed. The Friedman method was chosen, since overall it provided the best fit values and activation energies for FOX-7 of 90 kJ mol^{-1} and for FOX-7-D_4 of 225 kJ mol^{-1} were obtained. The previously made assumption that the activation energy for deuterated compounds is higher could therefore be confirmed experimentally.

All performed quantum chemical calculations are explained in more detail in the SI. Table 1 shows the results of the various calculations. Because the W1BD method is the most accurate one, only the results obtained using this method will be discussed in more detail. The zero-point energy of FOX-7 (237.3 kJ mol^{-1}) is higher than that of FOX-7-D_4 (202.6 kJ mol^{-1}) in agreement with the expectation that deuterated compounds show lower ZPEs than the non-deuterated analogue. The calculated HOF of FOX-7-D_4 (−114.0 kJ mol^{-1}) is also lower than that of FOX-7 (−91.0 kJ mol^{-1}). Calculations of the detonation

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Table 1. Heat of formation and zero-point energy calculation of FOX-7 and FOX-7-D_4.

	method	$-H^{298}$ [a] /a.u.	$\Delta_f H°(g)$ [b] /kJ mol^{-1}	$\Delta_f H°(s)$ [c] /kJ mol^{-1}	ZPE [d] /kJ mol^{-1}
FOX-7	CBS-4M	597.60	+ 12.1	− 82.2	257.2
	CBS-QB3	597.55	− 15.3	− 109.6	241.9
	W1BD	598.54	+ 3.30	− 91.0	237.3
FOX-7-D_4	CBS-4M	597.62	− 7.2	− 106.5	218.2
	CBS-QB3	597.57	− 33.2	− 133.0	206.5
	W1BD	598.55	− 14.7	− 114.0	202.6

[a] Electronic enthalpy; [b] Gas phase enthalpy of formation; [c] Standard solid state enthalpy of formation calculated by applying Trouton´s rule[12]; [d] Zero-point energy.

parameters in this case would be very interesting but they are ongoing, since no code is available for the calculation of deuterated explosives now.

In conclusion in this work, FOX-7 was deuterated to form FOX-7-D_4. The deuteration level was determined to be greater than 95% by ^{1}H q-NMR. Furthermore, it was possible to determine the crystal structure of FOX-7-D_4, it unexpectedly crystallized in a different space group than the non-deuterated FOX-7. The structures of both compounds were compared and discussed. In addition, the thermal stability was compared, here it was found that the deuterated FOX-7-D_4 exhibiting a decomposition temperature 30°C higher than the hydrogenated form. Moreover, the activation energy of thermal decomposition of both compounds was determined, as well as the enthalpies of formation and zero-point energies of both were calculated using different methods. Here it was shown that the previously established theory that deuterated compounds, in contrast to their hydrated derivatives, have a lower zero-point energy but a higher activation energy also applies to *N* deuterated compounds. For future studies, it would be definitely interesting to calculate the energetic parameters such as detonation velocity or detonation pressure for deuterated compounds, or in general for isotopically labeled compounds, to see how isotopic labeling affects the performance properties.

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Conflicts of interest

There are no conflicts to declare.

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