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Technical report

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Mass Spectrometric Study on FOX-7 Decomposition

Abstract (not more than 200 words)

The decomposition of FOX-7 has been studied by means of Time of Flight Mass Spectrometry (TOF-MS). The FOX-7 samples have been introduced into the MS via a heated solid sample probe. In addition to raw FOX-7, both deuterated and ^{15}N-labelled (nitrogroups only) FOX-7 have been used as sample material. The method for deriving the labelled material is included in the report. The use of labelled material gives conclusive information about the atomic composition of two identified EI-induced fragments, m/z 86 and 69. A modification of the TOF-MS setup that allows thermal decomposition studies with larger sample amounts, better resembling the conditions of Thermo Gravimetry, TG, and Differential Scanning Calorimetry, DSC, is presented.

Keywords
mass spectrometry, FOX-7, decomposition, isotopic labelling

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Masspektrometrisk studie av FOX-7's sönderfall

Sammanfattning (högst 200 ord)

Sönderfallsprodukter från FOX-7 har studerats med en Time of Flight-masspektrometer (TOF-MS). En uppvärmd fastfasprob användes för att introducera provet i masspektrometern. Förutom råmaterial av FOX-7 användes både deuterad och ^{15}N-märkt (nitrogrupperna) FOX-7 som provmaterial. I rapporten beskrivs den metod som använts för att framställa isotopmärkt FOX-7. Det isotopmärkta materialet ger avgörande information om den atomära sammansättningen av två identifierade EI-fragment, m/z 86 och 69. En modifiering av TOF-MS-uppställningen som möjliggör sönderfallsstudier med större provmängd presenteras. Modifieringen ger bättre överensstämmelse med experimentella förutsättningar för Thermo Graviometry, TG, och Differential Scanning Calorimetry, DSC.

Nyckelord
masspektometri, FOX-7, sönderfall, isotopmärkning

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Exekutiv sammanfattning

Utvecklingen av nya explosivämnen kan grovt delas in i två olika kategorier – bättre prestanda eller lägre känslighet. FOX-7 tillhör den senare kategorin – det har en låg känslighet i kombination med prestanda jämförbar med RDX. Dessa egenskaper gör att intresset för FOX-7 är stort. Mycket arbete har lagts ned på att karaktärisera FOX-7 för formulering och för indata till beräkningsmodeller (initiering, säkerhet, prestanda). Bland de metoder som använts finns röntgenkristallografi, DSC (Differential Scanning Calorimetry) och TG (Thermo Graviometry) som alla ger information i ett övergripande, makroskopiskt perspektiv. För att ännu bättre förstå de processer som bestämmer ett explosivämnes egenskaper behöver dessa metoder kompletteras med ett mikroskopiskt perspektiv, där reaktioner ända ned på molekylär nivå studeras. Ett sätt att göra detta är genom masspektrometri – en Time of Flight masspektrometer (TOF-MS) kan avslöja de reaktioner som pågår i en sönderfallsprocess.

Ett explosivämnes sönderfallsvägar ger viktig information om initieringsprocesser och om de förändringar i explosivämnet som kan uppstå till följd av uppvärmning eller kraftiga stötar. De kan t ex avslöja om ett explosivämne har en förhöjd risk att undergå autokatalytiska förändringar, eller om det vid ett långsamt termiskt sönderfall kan bildas instabila mellanprodukter. Att bestämma sönderfallsvägar är en omfattande och tidsödande uppgift, men varje nytt bidrag till den samlade kunskapen är viktigt.

Genom att utnyttja såväl råmaterial av FOX-7 som isotopmärkt material (deuterat och 15-N-märkt FOX-7) har det varit möjligt att entydigt identifiera sönderfallsfragment som utgör de två första stegen i en sönderfallskedja. Detta resultat visar på styrkan i kombinationen av masspektrometri och isotopmärkt material. De aktuella fragmenten härrör med största sannolikhet från den joniseringsprocess som använts vid de masspektrometriska mätningarna.

För att få ytterligare information ur TOF-MS-försöken är det möjligt att framöver byta EI-joniseringen mot laserjonisering (LIMS). Det annorlunda fragmenteringsmönster som då uppstår kan ge ledtrådar om vilka övriga fragment som är av termiskt ursprung och vilka som bildats till följd av joniseringen.

En framtida utmaning är att frysa in sönderfallsprodukter i en ädelgasmatris vid mycket låg temperatur - 6,5 K – och utföra matrisisolationsspektroskopi. Det blir då möjligt att analysera sönderfallsprodukter med ett flertal metoder, såsom IR- och Raman-spektroskopi och laserinducerad fluorescens (LIF). Resultatet kan bli en exakt identifiering av en mångfald produkter.

Index

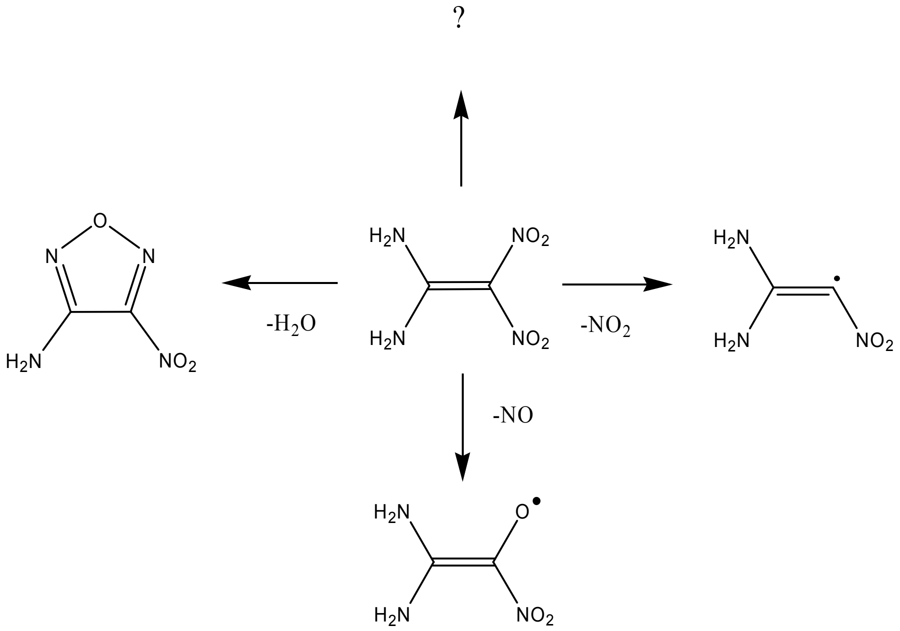
Decomposition of FOX-7 – a mass spectrometric study

Introduction

The development of new explosives can roughly be divided into two main categories - better performance or lower sensitivity. FOX-7 is of the second category - it has a low sensitivity combined with a performance close to that of RDX. This combination is the reason for the attention that is and has been directed towards FOX-7 since it was first synthesized at FOI in 1998[1]. In order to gain further knowledge about the formulation characteristics and modelling parameters of FOX-7, there have been a number of macroscopic characterization studies, i. e. crystallography[2], Differential Scanning Calorimetry[3,4] (DSC) and Thermo Graviometry[4,5] (TG). These types of studies need to be complemented with microscopic studies to create a better understanding of the characteristics of an explosive. A powerful tool for this is the Time of Flight Mass Spectrometer, which can reveal the molecular products formed in the decomposition process. The decomposition pathways tells much about the initiation process and the transformations that may occur in an explosive when exposed to heating or shock. They can reveal risks of autocatalytic reactions or unstable intermediates. They also present a possibility to fully understand the properties measured with the macroscopic methods. The quantum chemical models, which also play an important role in this area, need the experimental verification of decomposition pathways to be fully reliable. Experimental work and theoretical modelling should go hand in hand to get the best science in this field as in any.

To give further strength to the deduction of molecular decomposition products, measurements have been carried out on isotopically labelled FOX-7. The change in the mass spectrum from the same fragment, but of different isotopic constitution, gives a specific fingerprint that may be conclusive as to the atomic composition of the fragment.

The thermal decomposition of FOX-7 has been of interest to other research groups and quantum chemical calculations have been performed to conclude possible decomposition pathways. The suggested first step of the thermal decomposition is the loss of Nitric Acid (HNO_3)[6], the loss of water (H_2O)[7] or the loss of Nitrogen Dioxide (NO_2)[7]. It may be possible for two or more of the suggested first steps to be present at the same time. An overview of the first step in these decomposition pathways is found in Scheme 1.



Scheme 1: *The first step in some possible thermal decomposition pathways of FOX-7.*

Experimentals

The results presented in this paper are from measurements by a high resolution Time of Flight Mass Spectrometer (TOF-MS), which for this purpose has been equipped with a heated solid sample inlet. This makes it possible to use this specific TOF-MS with either conventional heating of a sample or pulsed CO_2-laser heating. Some earlier measurements have been done with laser heating[5], but the comparison between the results from the two heating methods is left for future studies. The ionization method used in the experiments on FOX-7 is Electron Ionization (EI), but the Mass Spectrometer can also be used with Laser Ionization (LIMS), using a laser operating at UV wavelenghts. An outline of the experimental setup is shown in Figure 1.

The TOF-MS is a Comstock, RTOF-210/EII, equipped with CP-625C/50F Microchannel plates for ion detection. It has a mass resolution of ~300 in linear mode. During the experiments, the background pressure in the extraction chamber was ~$5 \cdot 10^{-7}$ mbar and in the flight tube ~$1 \cdot 10^{-7}$ mbar. An Ortec Fastflight Digital Signal Averager was used for data collection.

The sample was introduced into the vacuum chamber via the heated solid sample inlet. This inlet was originally part of a JEOL 300D magnetic sector mass spectrometer, but has been modified to fit the TOF-MS. The heating of the inlet follows preset temperature programs. A diagram showing the temperature variation over time for these programs is found in appendix A. The temperature refers to the heater cartridge, the sample may have a slightly lower temperature.

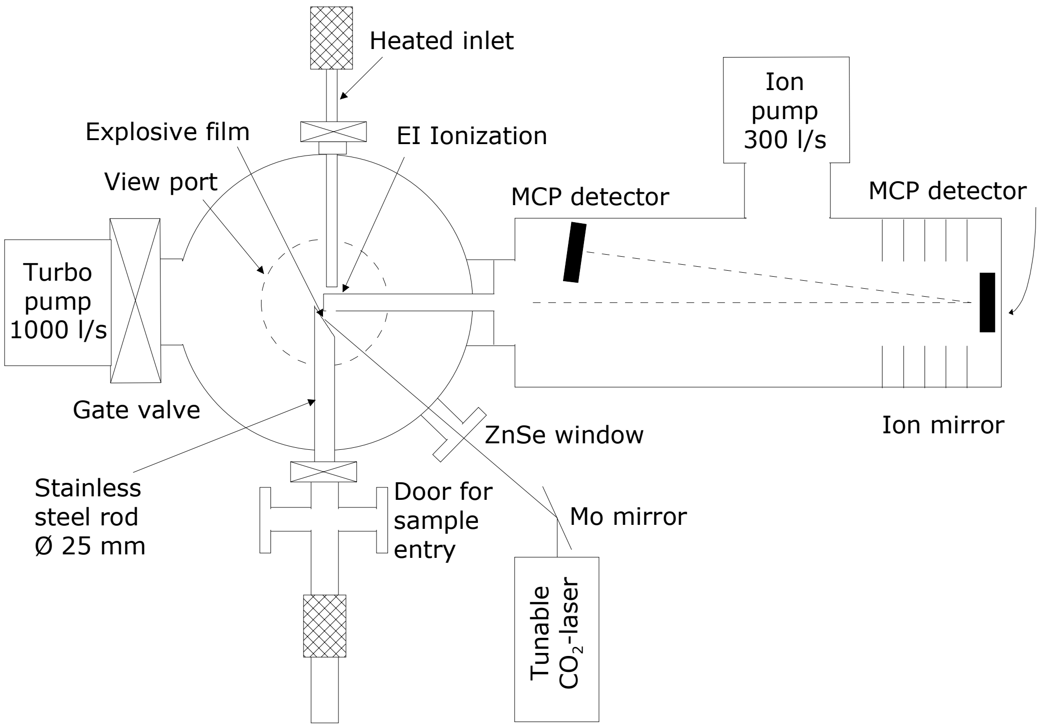


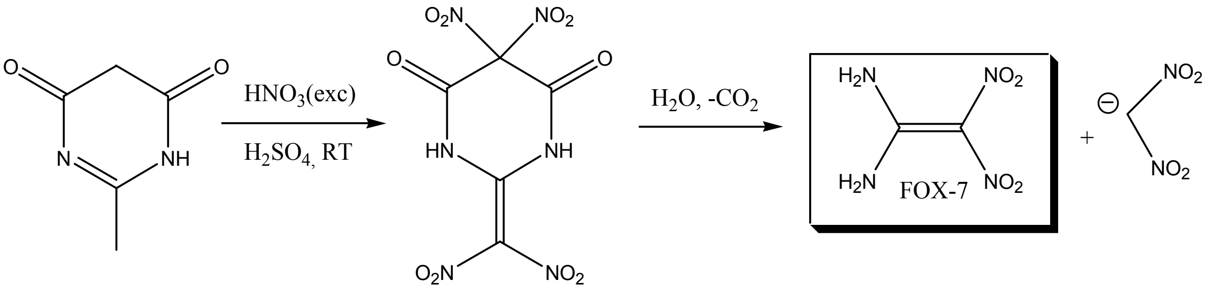
Figure 1: *Schematic drawing of the mass spectrometer set-up.*

A number of measurements have been carried out on the raw product of FOX-7 using the described experimental setup and criteria. The ionization method used is EI. The use of the Fastflight digital signal averager makes it possible to perform consecutive mass spectrometric measurements during an interval of several minutes, using the chromatography mode. In this way, the variation of spectra with time, and hence temperature, can be studied.

Measurements have been made on unlabelled as well as deuterated and 15-N labelled FOX-7. The ionization energy level has been varied between 20eV and 150eV for FOX-7 and 15-N labelled FOX-7, while the deuterated material has been studied only at the 70eV ionization energy level.

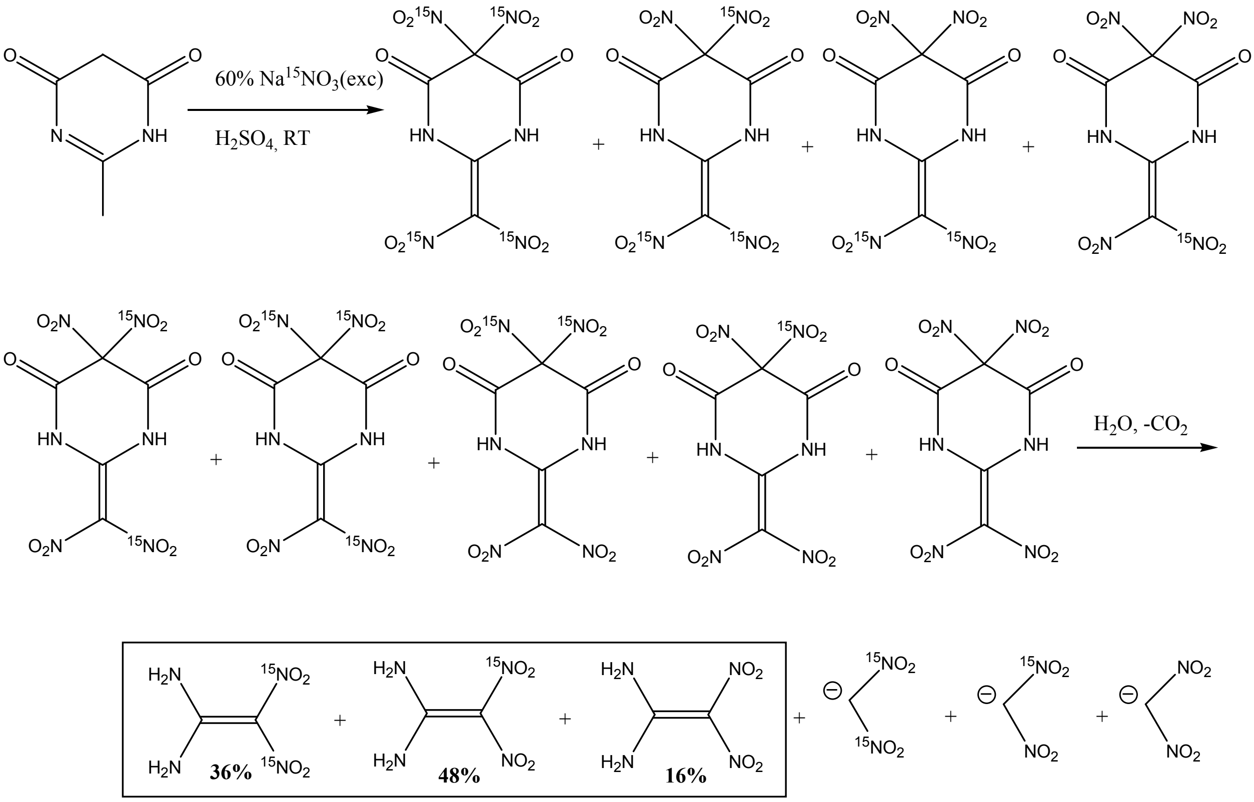
Preparation of 15-N labelled FOX-7 derivatives

The current commercial production method for FOX-7 is based upon the nitration of 2-methyl-pyrimidine-4,6-dione in mixed acids at room temperature. The reaction leads to the precipitation of 2-dinitromethylene-5,5-dinitro-dihydro-pyrimidine-4,6-dione, which is easily hydrolysed in water to FOX-7 and dinitromethane, see Scheme 2. [8,9]



Scheme 2: *Commercial production of FOX-7*

The simplicity of the reaction makes it useful for the introduction of 15-N labelled nitrogroups in FOX-7. Due to the use of 60% 15-N labelled KNO_3 a complex mixture of 9 differently labelled 2-dinitromethylene-5,5-dinitro-dihydro-pyrimidine-4,6-diones was produced. This mixture was however easily hydrolysed in water to FOX-7 and the corresponding mono and dinitro 15-N labelled analogues, see Scheme 3.



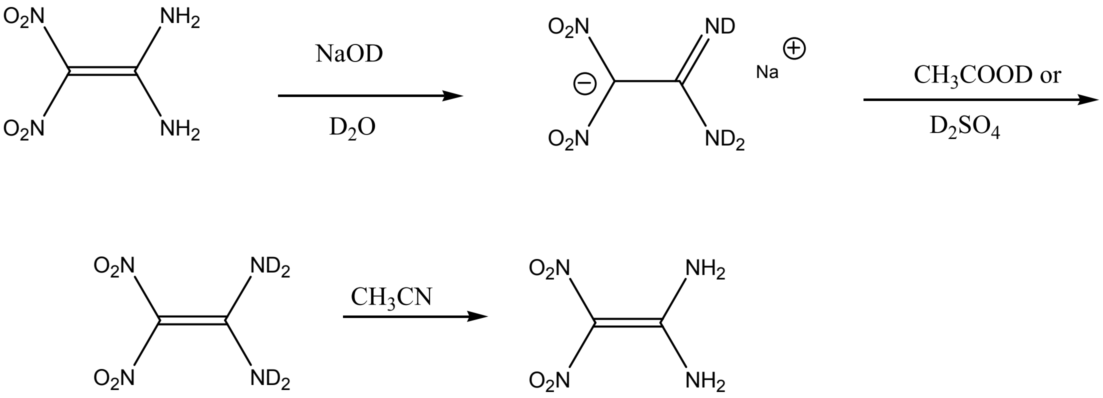
Scheme 3: *Preparation of 15-N labelled FOX-7*

Synthesis of 15-N labelled FOX-7

0.5 g (4 mmol) of 2-methyl-pyrimidine-4,6-dione was dissolved in 10 ml of sulphuric acid (95%). 1.7 g (20 mmol) sodium nitrate (60% 15-N) was added in portions. The reaction was stirred for forty minutes, whereupon the intermediate 2-dinitromethylene-5,5-dinitro-dihydro-pyrimidine-4,6-diones precipitated. The reaction mixture was added to 30 ml of cold water and stirred for 40 minutes. After hydrolysis the final product precipitated. It was filtered and washed 3 times with TFA . The product was 310 mg (2.1 mmol, 52%) of 15-N labelled FOX-7. The water phase was extracted with 50 ml of diisopropylether and 2.5 ml of 1M potassium hydroxide in methanol was added to the organic phase until a pH of 6 was obtained. The solution turned yellow and a further product precipitated. This was 146 mg (1.01 mmol, 25%) of 15-N labelled potassium dinitromethane.

Preparation of deuterated FOX-7

Under basic conditions in aqueous solutions FOX-7 shows rapid proton exchange. FOX-7 was dissolved in NaOD/D_2O and the fully deuterated compound was precipitated out of solution with acetic acid-d_1 or sulphuric acid-d_2. In acetonitrile the product quickly exchanged deuterium for hydrogen again, see Scheme 4. [10]



Scheme 4: *Preparation of deuterated FOX-7*

Synthesis of deuterated FOX-7

0.1 g FOX-7 was dissolved in 5 % NaOD solution to induce proton exchange. FOX-7 was then precipitated out of the solution with 96 % acetic acid-d. The product was then removed by filtration and dried at 40° C. 0.1 mg of the deuterated FOX-7 was then dissolved in 1 ml methanol-d and analysed using mass spectrometry. MS m/e 152 (M^+). The product was also analysed using NMR, ^1H NMR (DMSO-d_6) δ 9.06 ppm.

Results

A typical chromatogram of FOX-7, see Figure 2, shows some interesting features. Three regions of more prominent ionic activity can be seen. This tendency of varying amounts of reaction products with time, and thus heating temperature, shows similarities to earlier TG and DSC measurements[3,4,5], but the temperature reading of the solid probe heater used in the TOF-MS is not accurate enough for any certain conclusions. The amount of material used in the mass spectrometer is also very much smaller than the amount used in TG, making direct comparisons risky. However, the experimental setup can be altered to better fit the experimental circumstances of TG and DSC, as will be discussed.

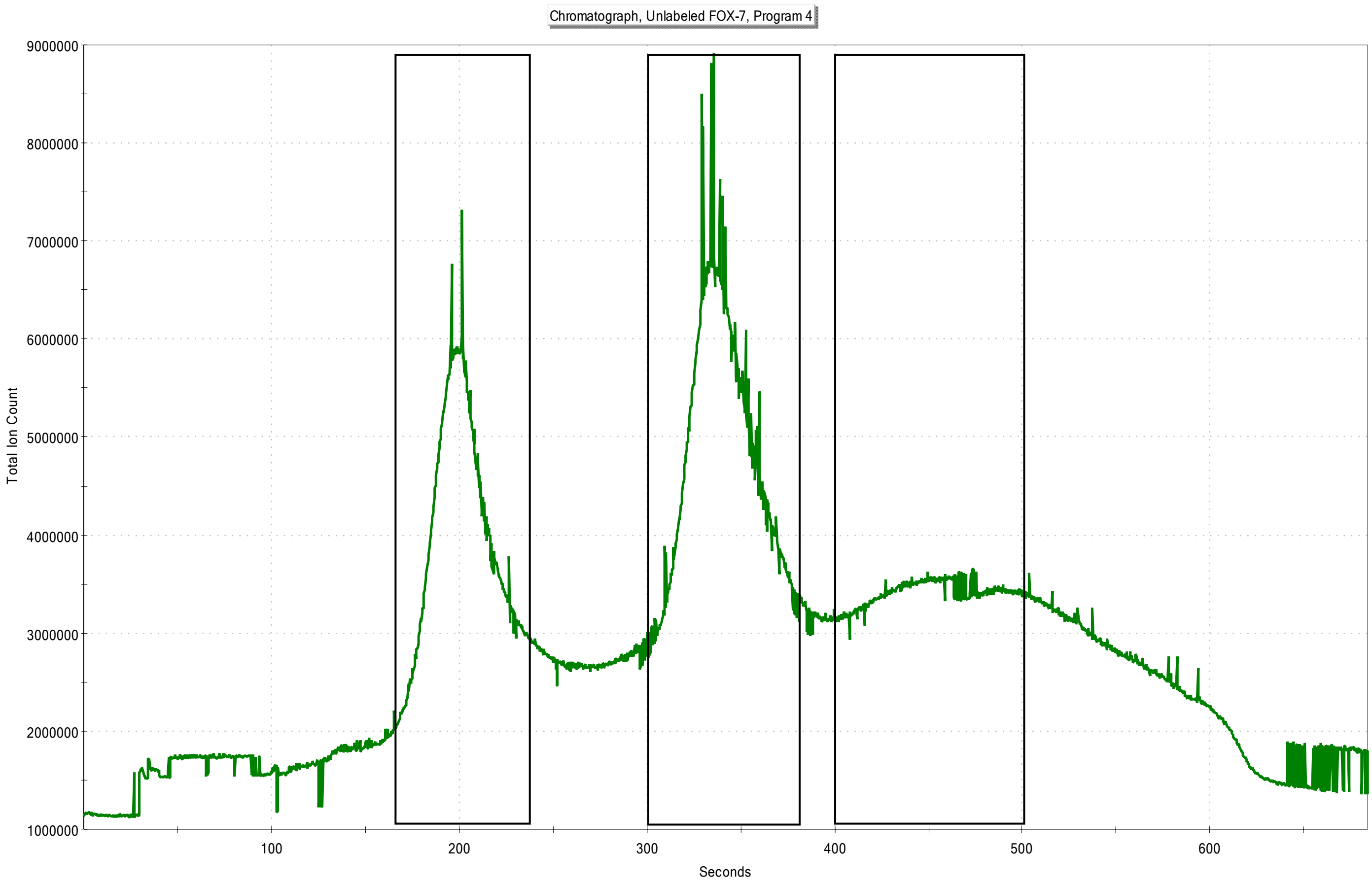


Figure 2: *Chromatogram from an experiment using heating program 4 and using relatively much material to make the regions of high total ion count more pronounced.*

A close examination of the mass spectra from different time (temperature) regions shown in Figure 3 reveals a difference in the relative intensity of the molecular ion at *m/z* 148 to the ions in the lower *m/z* region of the spectra. The *m/z* 148 ion increases significantly with time (temperature). It can also be seen that as the intensity of *m/z* 148 increases, three other *m/z* values have the same tendency. These are *m/z* 86, *m/z* 69 and *m/z* 43.

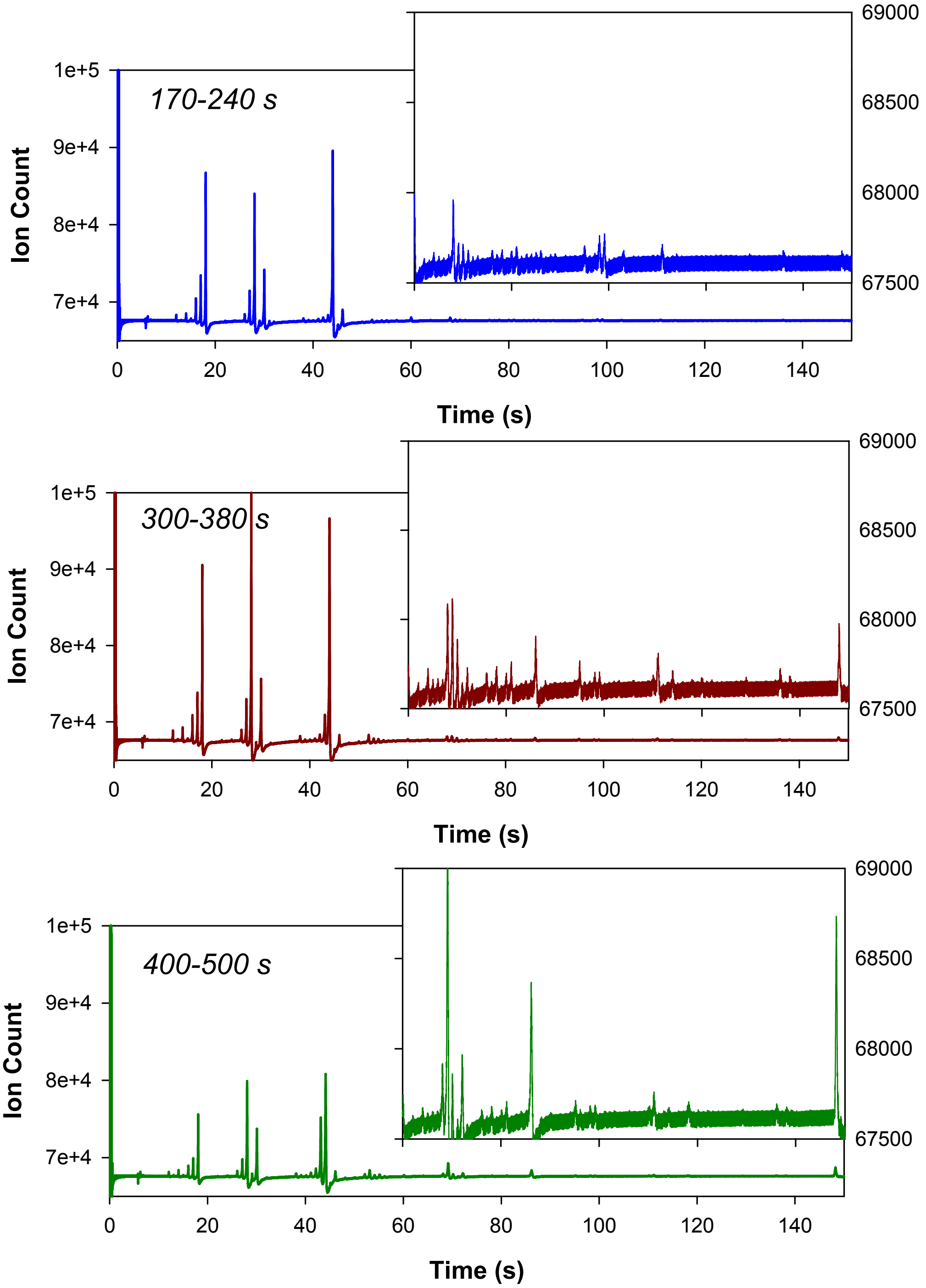
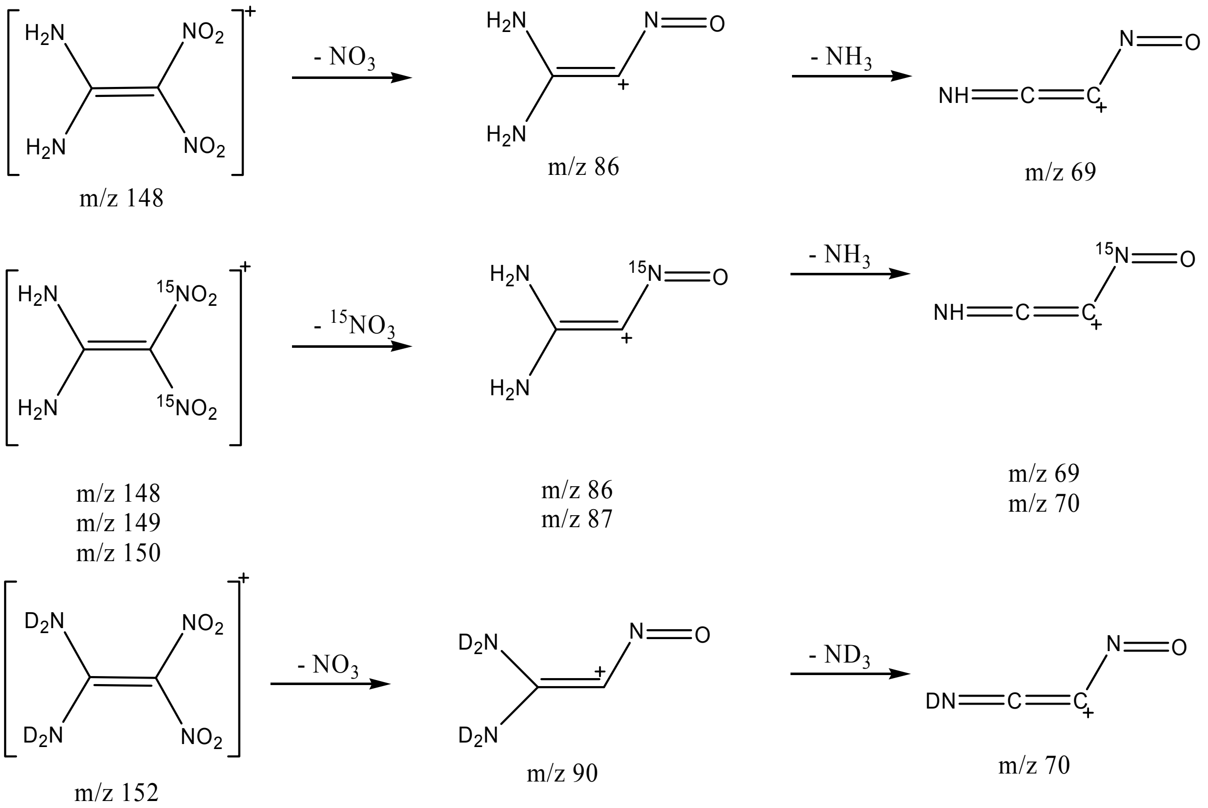


Figure 3: *Mass spectra at different times (temperatures) show that the molecular ion grows more than some of the lower mass ions. 170-240s: The molecular ion, m/z 148, and the fragment ions of m/z 86 and 69 are not present. 300-380s: As the full molecular ion appears (m/z 148), the m/z 86 and 69 ions are also appearing in the spectrum. 400-500s: m/z 148 has grown in intensity and m/z 86 and 69 follow the same pattern. This is also true for the ion of m/z 43. The higher mass region of the spectra has been enlarged for clarity. Heater program 4 was used for these measurements.*

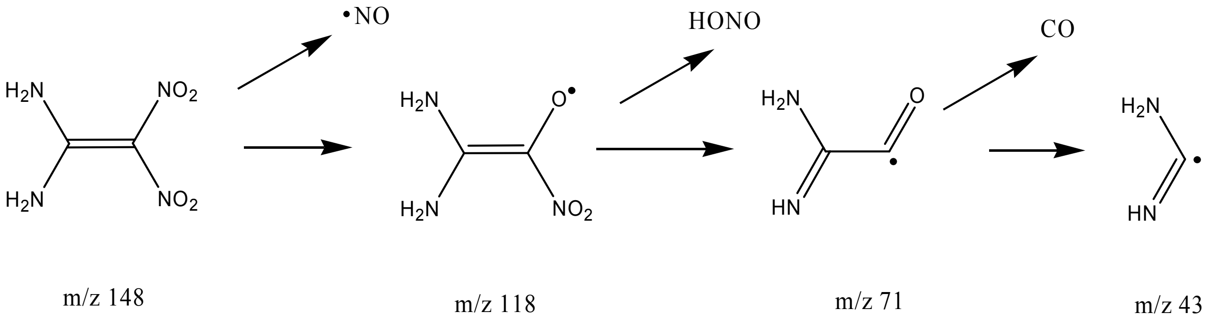
A possible explanation is that thermal processes dominate in the earlier (lower temperature) mass spectra and that as the temperature rises, more FOX-7 is evaporated off the sample and subsequently ionized by EI. If this is the case, it is a reasonable conclusion that the origin of the peaks that increase in intensity together with the molecular ion is electron impact ionization. This conclusion is further supported by the observation that the intensity variations of the *m/z* 86, *m/z* 69 and *m/z* 43 seem to closely follow that of the molecular ion *m/z* 148.

As seen in Scheme 5, data from labelled FOX-7 measurements give important information about the molecular structure of these fragments. Figure 4 shows typical data from the later stages of the heating procedure for FOX-7, D FOX-7 and 15-N FOX-7 respectively. The molecular peak at *m/z* 148 splits into three peaks with *m/z* 148, 149 and 150 in the ratio 0.16:0.48:0.36 with 15-N-labelling and it shifts to *m/z* 152 with deuterated material. This is fully consistent with 60% of the nitrogroups being labelled and a deuteration of 100%. Speculations regarding the origin of the peak at *m/z* 86 have been made before[5]. The fact that it shifts to *m/z* 90 with deuterated material and splits in two with *m/z* 86 and 87 (0.4:0.6) with 15-N-labelled material now pinpoints this fragment since it *must* have four hydrogens and one remaining nitrogen from the nitrogroups. The origin of the peak at *m/z* 69 is also quite clear from the labeled measurements. This peak splits in two with *m/z* 69 and 70 (0.4:0.6) with 15-N-labelled material and shifts to *m/z* 70 with deuterated material. The origin of m/z 43 is yet to be determined.



Scheme 5: *Suggested EI-induced decomposition of FOX-7.*

A calculated thermal decomposition pathway, as presented in Scheme 6, can be found in the literature[8]. Our experimental data can not confirm this decomposition pathway, that is, there are no significant peaks at m/z 118 and m/z 71 representing the first fragments of this decomposition pathway. However, a more thorough study may reveal these or other interesting fragments present in a different time/temperature interval.



Scheme 6: *Thermal decomposition of FOX-7 as calculated by Gindulyte at al.*[11]

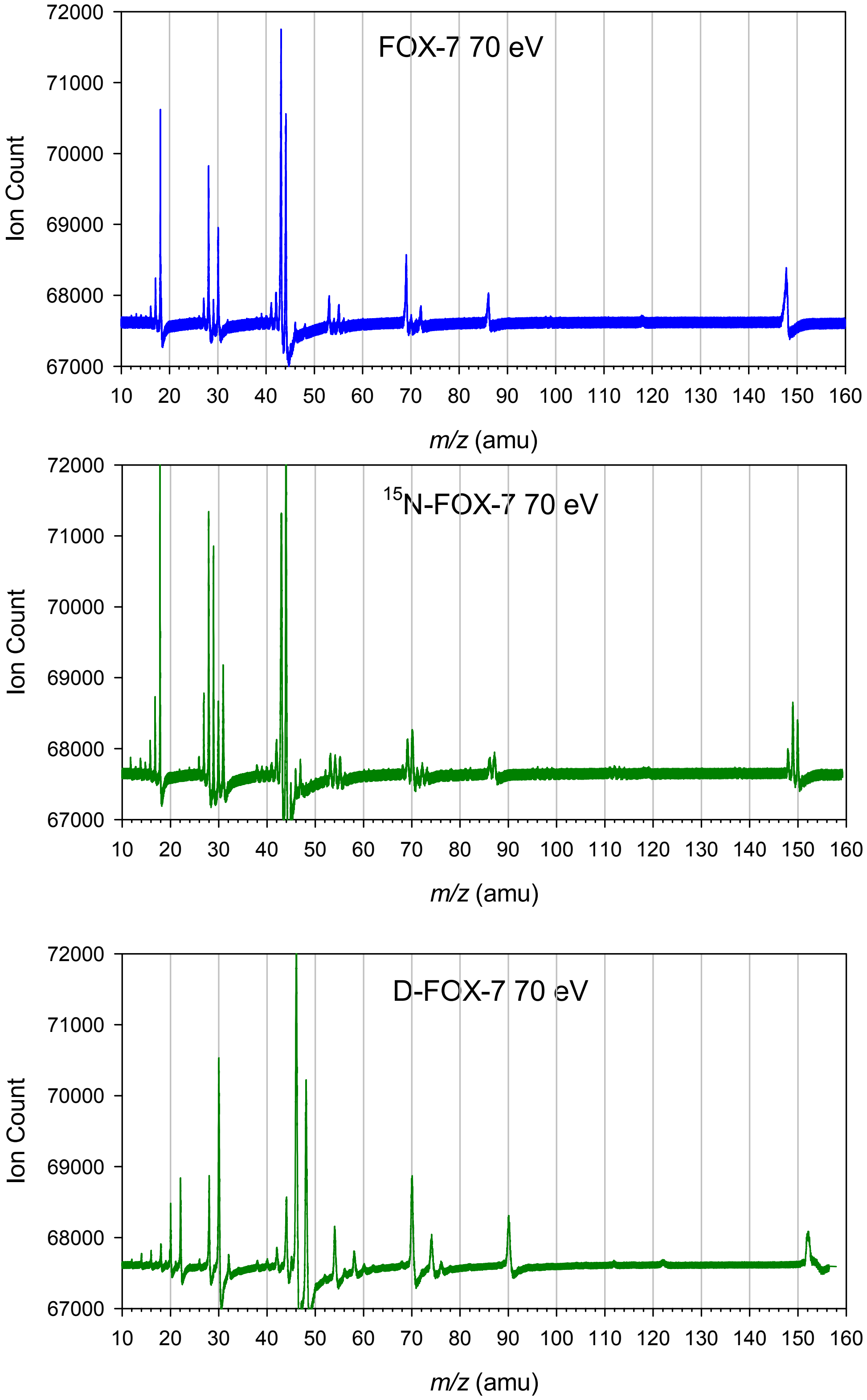


Figure 4: *Mass spectra of FOX-7 without isotopic labeling, with 15-N-labeling on the* NO_2*-groups (40:60) and deuterated FOX-7. The deuterated FOX-7 measurement was made with heater program 4, the others with program 6.*

Variation of ionization energies leads to the conclusion that FOX-7 is a stable molecule with respect to electron impact. At EI levels of 150 eV, the molecular ion is still as prominent as with EI levels of 70 eV (Figure 5). It might be noted that care should be taken when data collected with this TOF mass spectrometer are compared to those registered on other instruments since the ionization chambers differ and the resulting mass spectrum of the same ionization energy might not be completely in agreement.

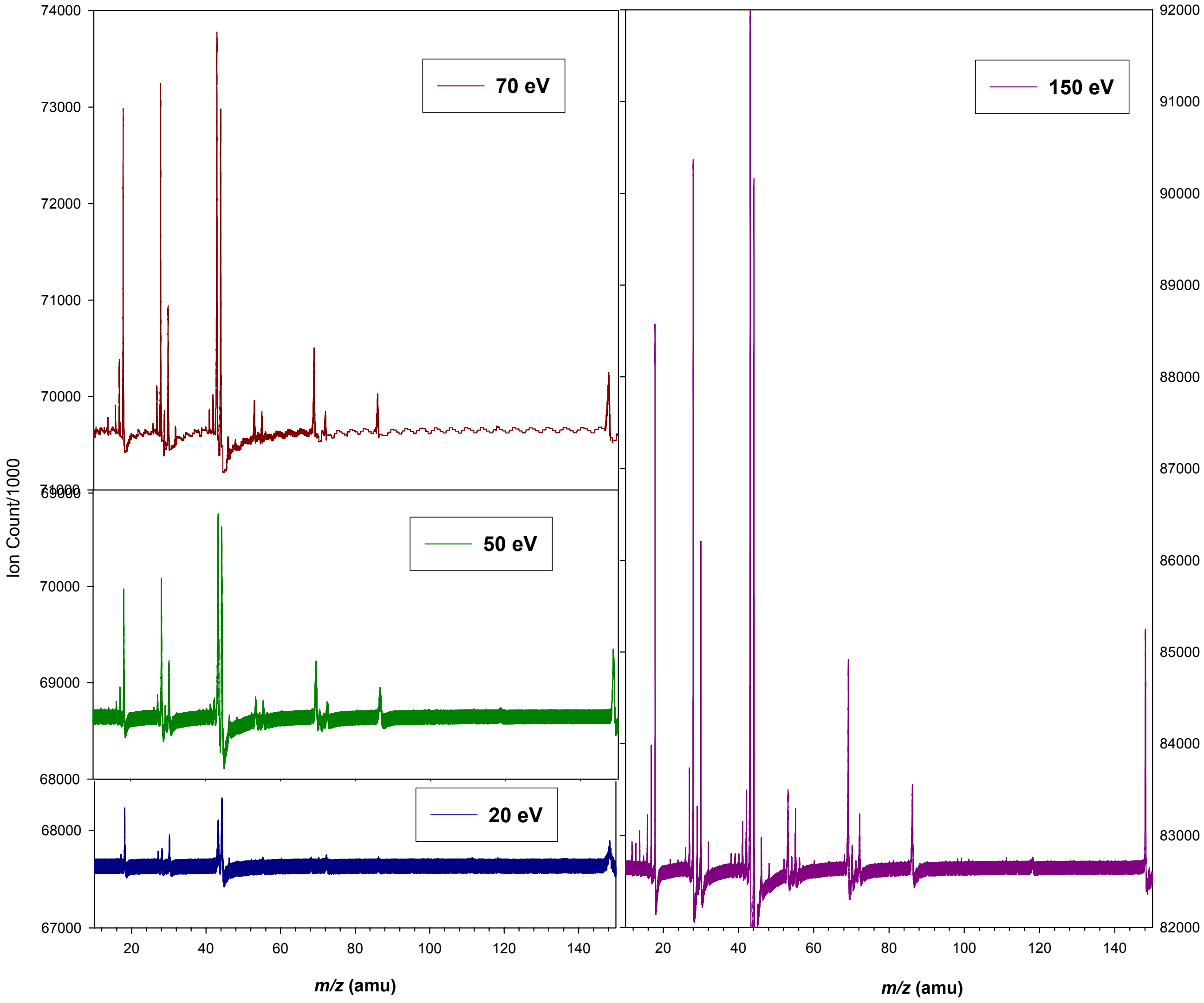


Figure 5: *Mass spectra of FOX-7 at different ionization energies using heater program 6.*

Conclusion and near future plans

The use of labelled material in decomposition studies has proven to make a significant contribution to the identification of the produced fragments. Although the mass spectrum of the raw material gives important information in itself, the use of isotopically labelled material can in some cases give conclusive information about the atomic constitution of a fragment. This is indeed the case with the EI induced fragments of FOX-7 with *m/z* values 86 and 69, which have proven to be $C_2H_4N_3O$ and C_2HN_2O respectively. Labelled material will play an important role when the studies of FOX-7 are directed towards experimental analysis of thermal decomposition pathways.

To be able to closer investigate the thermal decomposition of FOX-7, and doing this in a way that closer resembles the experimental conditions of TG and DSC measurements, the TOF-MS setup will be modified. The sample will be placed outside the MS and held at a constant elevated temperature (up to 200°C). The thermal products will then flow through a deactivated fused silica capillary (GC-type) into the ionization chamber of the MS. By placing the sample outside the MS, a larger sample can be used without causing an elevated pressure inside the MS. This enables measurements during longer time intervals, revealing more detailed information about the processes involved at specific temperatures. The temperature regimes of greatest interest can be identified from reported DSC and TG measurements. If the EI decomposition products should dominate the mass spectra, EI ionization can be replaced by laser ionization. This will not solve the problem of having decomposition from the ionization process, but the probable difference in ionization fragmentation will contribute in the process of finding out the origin – thermal or ionization induced - of the registered decomposition products.

As a complement to TOF-MS studies on decomposition, the possibility to use matrix isolation spectroscopy is closely considered. The method allows the decomposition products to be stored in a matrix at a temperature of 6.5 K and investigated by means of different spectroscopic methods such as IR-spectroscopy, Raman-spectroscopy or the highly sensitive Laser Induced Fluorescence (LIF). Another advantage of the matrix isolation method is that it may probably be used for studies of shock induced initiation products by laser initiating the explosive when in the matrix.

Acknowledgement

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APPENDIX A

Diagram of heater programs

Temperature (°C) vs. time (minutes) curves for the heated inlet. Numbers in circles refer to program number.