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Relative partial cross sections for anions formed upon electron attachment to nitrotoluene

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Abstract

Free electron attachment to the three different isomers of mono-nitrotoluene molecules in the gas phase is studied using a crossed electron-molecule beams technique. For the molecule 2-nitrotoluene 77 products anions are measured. The ion yield of the different anions spans a range of more than six orders of magnitude. The total anion yield of the three different isomers of mono-nitrotoluene is compared and shows remarkable differences mainly resulting from the different contributions of the NO_2^- fragment anions. The anion efficiency curves show six resonances that we assign to different transient negative ions. Competition of decay reactions is forming a series of fragment anions from each isomeric transient negative anion.

Keywords: Nitrotoluene; Electron attachment; Partial cross section

1. Introduction

Nitro-organic compounds are molecules with a significant potential for the industrial use, particularly as explosives or propellant. 2-Nitrotoluene (*o*-MNT) and 4-nitrotoluene (*p*-MNT) are used as tagging agents for plastic explosives. These molecules are intermediate products for the synthesis of pesticides, drugs, dyestuffs and synthetic materials. 2-Nitrotoluene is found in explosives for mining and is an intermediate product in the synthesis of trinitrotoluene. Among the nitro compounds, explosives such as trinitrotoluene form a group of chemicals of considerable interest for environmental and analytical chemistry [1]. Moreover the detection of explosives is a topic of increasing interest [2]. A wide variety of very sensitive methods have been developed for environmental analysis of explosives and/or their degradation products (see the review [3]).

Nitro compounds contain one or more nitro (NO_2) functional groups. These molecules possess very pronounced electron-acceptor properties due to the low energy of the lowest unoccupied (π^*) orbital of the NO_2 group. Low-energy electron interaction with nitro derivatives has been a subject of many studies [4–10]. Nitrobenzene and nitrotoluene were studied in the 1960s by Christophorou et al. [11] utilizing a swarm technique. Non-dissociative electron attachment to nitro compounds, forming long-lived molecular anions, as well as dissociative electron attachment, producing the nitro fragment anions NO_2^- (m/z 46), was observed in this work. Several studies have described that this nitro anion can serve as a fingerprint for the identification of the neutral compound [12–14] and thus its great potential as a marker for the detection of explosives [12,15]. Furthermore, Havey et al. [12] demonstrated by measuring the NO_2^- resonance energies for 25 different nitroaromatic compounds including several isomeric species that it is possible to distinguish structural isomers of nitro compounds, including the three isomers of mono-nitrotoluene. In a recent study by Sulzer et al. [7] differences between the anion efficiency curves of several other fragments upon DEA to the three isomers of mono-nitrotoluene was observed. Chen and Wu [16] and later Chen and Chen [17] performed computational studies about the stability

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and internal rotational barriers of the 3-nitrotoluene (NT) isomers. According to their calculations [16] the 4-NT is the most stable isomer and for 2-NT the steric effect between the nitro group and the methyl group leads to a torsional angle of the nitro group up to 22°. Both, experiment [7,12] and theory [16] find that the proximity of the nitro and the methyl group of the 2-NT leads to substantial differences between this isomer and the two other forms, i.e., 3-NT and 4-NT and only very small deviations between the latter two can be observed.

Although many other fragment anions besides the dominant NO_2^- upon DEA to nitro-organic compounds have been detected [4,5,13,14] in negative ion mass spectra these product anions have not been investigated concerning their anion efficiency curves. In [7] 55 common fragment anions of the three different isomers of NT were compared and besides the parent anion the relative cross sections of 10 anions are shown that exhibit differences for the three isomers. In the present study 77 anion efficiency curves for electron attachment to 2-nitrotoluene are shown and compared with respect to the relative yield of the six existing resonances.

2. Experimental setup

The present experiments are carried out using two-crossed electron–molecule beams instruments described previously in [18]. A high-energy resolution hemispherical electron monochromator in combination with a quadrupole mass filter is utilized to measure high intensity anions that exhibit narrow resonances close to 0 eV. The present measurements at this instrument are performed with an electron energy resolution of about 60 meV for the parent and NO_2^- anion and 120 meV for the anions with $m/z = 107$, 108 and 136. The corresponding electron currents are 5 nA and 20 nA, respectively. The second apparatus is a double focusing high-resolution two-sector field mass spectrometer equipped with a standard Nier-type ion source. The electron energy resolution close to 0 eV is about 1 eV and the electron current is regulated to 10 μA. This value is reached at electron energy of about 2 eV. The mass spectra at non-zero electron energy shown in Fig. 1 and all anion efficiency curves shown in this work except the ones mentioned above are measured with this instrument. The yield of the anions measured with the monochromator instrument is normalized with the wide resonances of the anions with $m/z = 46$, 107 and 136, measured with both instruments.

2-NT and 3-NT are under standard condition liquids with vapor pressures sufficiently high for the present experiment. 4-NT forms yellow crystals and require moderate heating of the gas inlet system to about 40 °C to obtain the same target density in the ion source, measured by a hot cathode ionization gauge. The samples are obtained from Sigma–Aldrich with a stated isomeric purity of >99% for the 2-NT and >98.5% for the 3-NT and 4-NT. The molecules pass a capillary (diameter of about 0.8 mm) located in front of the ion source and form an effusive molecular beam that is crossed by the electron beam. No extraction field is used in the monochromator instrument and the product ions leave the ion source with the effusive beam. Afterwards they are focused to the entrance of the quadrupole mass spectrometer. In the sector field instrument an ion repeller is pushing the ions out of the magnetic field that guides the electrons through the ion source. A voltage drop of 7 kV is accelerating the ions to the sector fields. In both instruments the mass selected negative ions are detected by a channeltron detector and the resulting pulses processed using a pulse counting technique and a computer. The intensity of a mass selected negative ion is recorded as a function of the electron acceleration voltage.

The electron energy scale is calibrated using the electron attachment reactions:

$$e + CCl_4 \leftrightarrow CCl_4^{-\#} \leftrightarrow Cl^- + CCl_3 \qquad (1)$$

and

$$e + SF_6 \leftrightarrow SF_6^{-\#} \qquad (2)$$

Both processes exhibit a narrow s-wave resonance at 0 eV. The apparent width of the resonance is used as a measure for the electron energy resolution of the electron beam.

3. Results

Negative ion mass spectra of 2-nitrotoluene measured at four electron energies, i.e., about 0 eV, 4 eV, 7.5 eV and 10 eV are shown in Fig. 1. These energies correspond to four major resonances that are common for several of the product anions. A logarithmic scale is used for the ion intensity that spans six orders of magnitude. At about 0 eV only NO_2^-, the parent

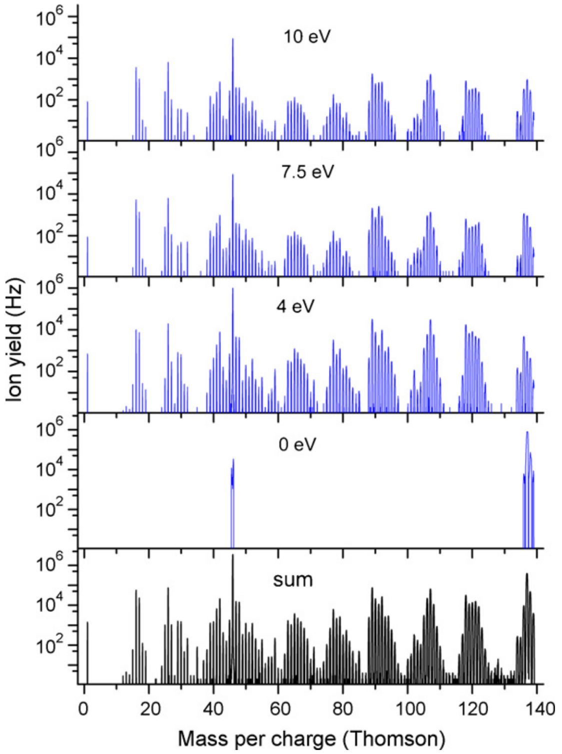

Fig. 1. Negative ion mass spectra of 2-nitrotoluene recorded at the electron energies of 0 eV, 4 eV, 7.5 eV and 10 eV. The electron current was set to 10 μA and the pressure in the ion source was 2×10^{-4} Pa. The lowest diagram shows a mass spectrum that has been obtained by summation of mass spectra measured at ten electron energies, i.e., from 0 eV to 9 eV in 1 eV steps.

and the dehydrogenated parent anion are formed in significant amounts. However, at the higher energy resonances all mass spectra show anions at almost every mass. At 4 eV most of the anions have their maximum ion yield. The rich fragmentation patterns observed for electron attachment to nitrotoluene suggest that the electronic energy of the core-excited resonances is randomly distributed among the vibrational degrees of freedom of the molecule. A similar strength of the different bonds in the molecule can explain the presently observed competition of the decay into so many different fragment anions. The only exception is the NO_2^- anion that is about 20 times more intense than all other fragments. Additional support for a complete randomization of the energy in the vibrational modes of the molecule is found in the presence of delayed unimolecular decomposition of several product anions. It is interesting to note that for TNT even at about 0 eV such a rich negative ion mass spectrum was reported [13]. The lowest panel in Fig. 1 shows a mass spectrum that was summed up over 10 electron energies (from about 0 eV to 9 eV in 1 eV steps). The non-zero eV mass spectra show several groups of peaks that can be assigned to anions that contain different numbers of heavy atoms, i.e., carbon, nitrogen and oxygen. In the mass range between 33 Da and 60 Da two groups are overlapping caused by the relatively heavy NO_2^- anion and its isotopomers that contain no hydrogen but close the gap to the C_4 group.

Fig. 2 shows the total anion efficiency curves for the three different isomers of mono-nitrotoluene. These curves were obtained via summation of all partial anion efficiency curves that could be measured within the limit of the sensitivity of the instruments. The isotopomers of the parent anion, resulting from ^{13}C, ^{15}N and ^{18}O are not shown explicitly but included in the total anion efficiency curves. At a resonance close to 1 eV electron attachment to 2-nitrotoluene is almost five times more efficient compared to the other two isomers. At all other electron energies the total anion efficiency curves of 2-NT and 3-NT are very similar. At electron energies higher than 4 eV 4-nitrotoluene differs from the other isomers and DEA is about three times more efficient. In a recent study [7] the anion efficiency curves of all individual anions that contribute to these differences are shown and discussed in detail.

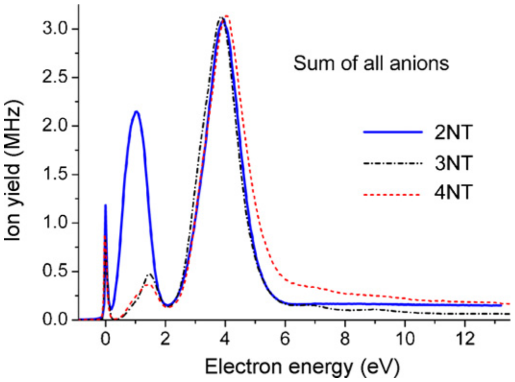

Fig. 2. Total anion efficiency curve upon free electron attachment to 2-nitrotoluene (solid curve). The pressure in the ion source was 2×10^{-4} Pa and the electron current was set to 10 µA. The values were obtained adding up all anion efficiency curves shown in Figs. 4–11. A comparison is made with the total anion efficiency curves for 3-nitrotoluene (dash-dotted line) and 4-nitrotoluene (dashed line).

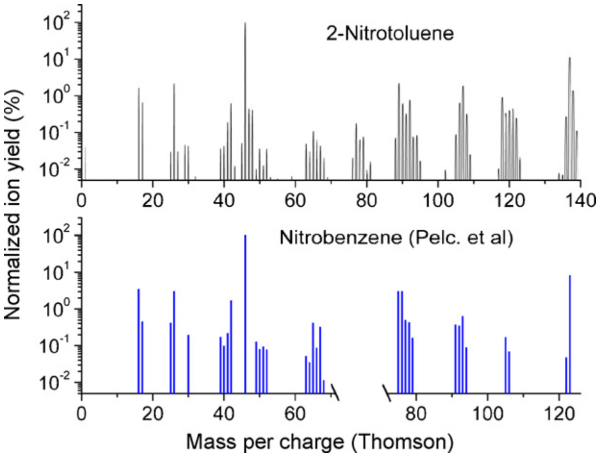

Fig. 3. Negative ion mass spectrum of 2-nitrotoluene (summed up over 10 electron energies) compared with the cross section values published by Pelc et al. [6] for nitrobenzene.

Fig. 3 compares the sum of the mass spectra measured at ten electron energies as shown in the lowest panel of Fig. 1 with the cross section values reported by Pelc at al. [6] for electron attachment to nitrobenzene. In contrast to the present study several anions were not measured such as the isotopomers of NO_2^- at the masses $m/z = 47$ and 48. There is very nice accordance between the mass spectra for the two-nitroaromatic compounds up to the mass groups containing five heavy atoms. For better comparison the mass scale of the nitrobenzene mass spectrum is broken after 70 Thomson and the higher part of the mass spectrum is shifted by 14 Thomson to align the two parent anions. Thereby the common nature of the first four mass groups becomes obvious which represents the preferential loss of oxygen and nitrogen for these fragments.

Figs. 4–11 show the anion efficiency curves measured for 77 masses upon electron attachment to 2-nitrotoluene. For all anions contributions from residual gas in the instrument and memory effects from substances prior to the measurements were checked and can be neglected. Only impurities in the sample itself may influence the present anion efficiency curves. All fragment anions exhibit a strong resonance close to 4 eV. The average position of this most intense resonance for nitrotoluene is at 3.99 ± 0.03 eV. It is quite remarkable that at such low electron energy fragments, such as H^-, C^- and small hydrocarbon anions that only can form upon fragmentation of the benzene ring are formed. The electron affinity of H is 0.75 eV [19]. The sum of the electron energy and this value is still too low to directly form H^- via a simple bond cleavage reaction:

$$e + M \rightarrow M^{\#-} \rightarrow [M\text{–}H]^{\bullet} + H^-. \quad (3)$$

Recent studies showed that the resonance energy for H^- formation via reaction (3) depends strongly on the element to which hydrogen is connected in the molecule [18,20,21]. For a carbon site this would lead to a resonance at around 10 eV [20,21]. The only explanation for the 4 eV resonance of H^- is a substantial rearrangement of the neutral fragments into more stable products.

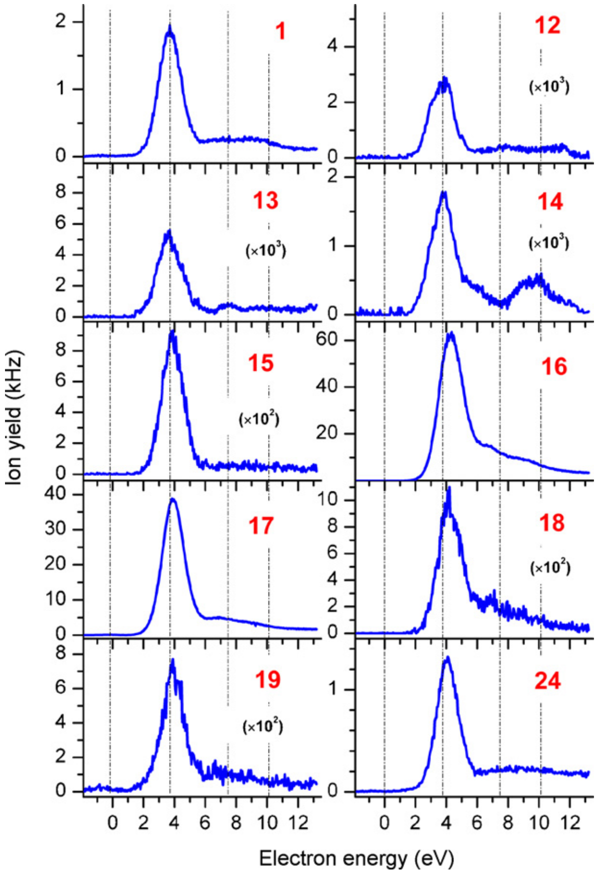

Fig. 4. Anion efficiency curves for the formation of anions with $m/z = 1$ to $m/z = 24$ upon dissociative electron attachment to 2-nitrotoluene. The electron current was set to 10 μA and the pressure in the ion source was 2×10^{-4} Pa. All anions were measured with the sector field mass spectrometer with an electron energy resolution of about 1 eV.

3.1. One heavy atom fragment anions (m/z = 12 to 19)

The masses with $m/z = 12$, 13, 14 and 15 can be assigned to CH_n^- with $n = 0 \ldots 3$. The anions with $m/z = 16$–19 correspond to O^- and OH^- with their isotopomers containing ^{18}O, respectively. The isotopic ratio $^{16}O/^{18}O$ and $^{16}OH/^{18}OH$ is 0.2%, which agrees quite well with the measured intensity ratios for the corresponding masses with 0.14% and 0.18%, respectively. In the literature several examples of isotope effects for DEA are described [22–24] and reach values up to 200 in case of H^- and D^- from H_2 and D_2, respectively [25]. Thus a slightly lower yield for the heavy isotopes than calculated from the isotopic ratios may be the result of an isotope effect.

3.2. Two heavy atoms fragment anions (m/z = 24–31)

The dominant anion in this mass range is $m/z = 26$. CN^- and $C_2H_2^-$ are possible candidates for this mass. The anion efficiency curve of $m/z = 27$ has the same shape and is almost two orders of magnitude less intense. Depending on the composition of $m/z = 26$ its isotopomer should be 1.5% (CN^-) or 2.2% ($C_2H_2^-$) of the main peak. In the present case the ratio of the intensity of $m/z = 27$ and $m/z = 26$ is 1.4% and indicates that CN^- is the dominant anion of this group. Furthermore, HCN^- does not contribute significantly to mass 27 in contrast to DEA to nitroethane [5]. Mass 25 is one of the few product anions that do not have the maximum of the anion efficiency curve at around 4 eV. It shows three resonances at 0 eV, 4.34 eV and 7.8 eV with a distinct shoulder at 10.7 eV. The anion efficiency curve of $m/z = 49$ has exactly the same structure with its maximum at around 8 eV. The only possible structures of these $m/z = 25$ and 49 are C_2H^- and C_4H^-, respectively. Both anions are energetically at 0 eV not possible as fragments of nitrotoluene. A careful check of contributions from the residual gas showed that the 0 eV peaks remain whereas the high-energy resonances are originating from DEA to nitrotoluene.

3.3. Three heavy atoms fragment anions (m/z = 38–48)

The dominant fragment anion formed via DEA to all isomers of mono-nitrotoluene and many other nitroaromatic compounds is the nitrogen dioxide anion NO_2^-. The NO_2^- ion yields for all isomers show two strong maxima at about 1.4 eV and 3.85 eV and weak resonances at 6.5 eV and 9 eV. The high-energy features are less pronounced for 2-NT which in contrast to the other isomers shows a narrow 0 eV resonance. According to electron

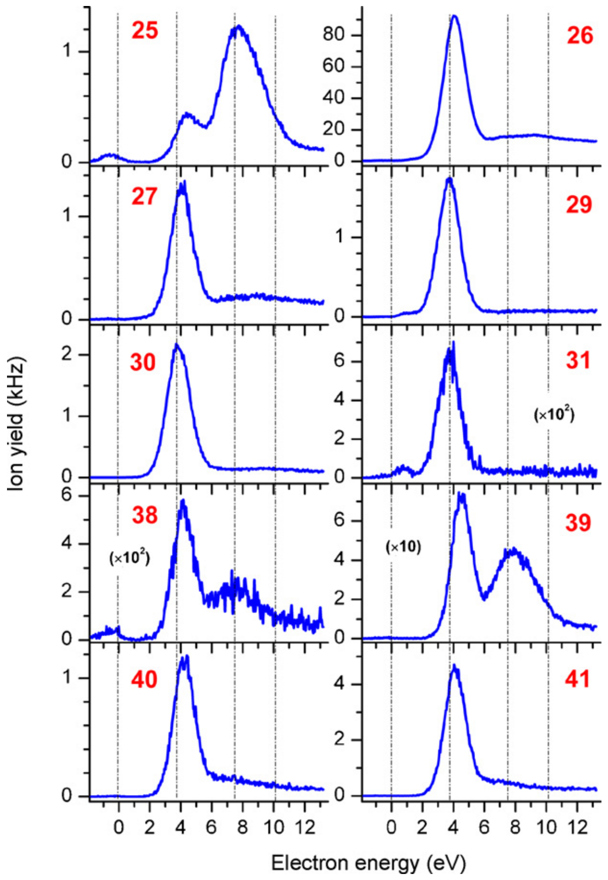

Fig. 5. Anion efficiency curves for the formation of anions with $m/z = 25$ to $m/z = 41$ upon dissociative electron attachment to 2-nitrotoluene. The electron current was set to 10 μA and the pressure in the ion source was 2×10^{-4} Pa. All anions were measured with the sector field mass spectrometer with an electron energy resolution of about 1 eV.

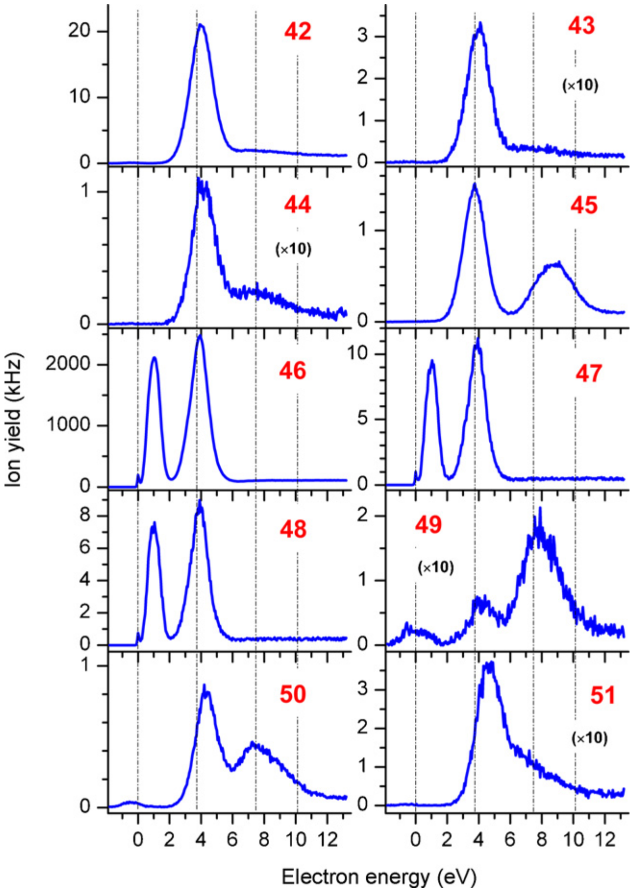

Fig. 6. Anion efficiency curves for the formation of anions with $m/z=42$ to $m/z=51$ upon dissociative electron attachment to 2-nitrotoluene. All anions were measured with the sector field mass spectrometer with an electron energy resolution of about 1 eV. The electron current was set to 10 μA and the pressure in the ion source was 2×10^{-4} Pa. The anions with $m/z=42$, 46, 47 and 48 were measured with the electron monochromator instrument with an electron energy resolution of 80 meV and the data were normalized to the sector field data at the 4 eV resonances of the anions. Only the anion efficiency curves measured with the monochromator instrument are shown for these masses.

transmission spectroscopy of nitro derivatives in the gas phase the peak at 1.4 eV is associated with simple electron capture into the π^* orbital (which has antibonding character between the nitro group and the ring), whereas signals at higher energies are associated with core-excited resonances [8]. From the C–N bond energy in nitrotoluene (obtained utilizing the G2MP2 method: 2-NT: 3.4 eV, 3-NT: 3.5 eV, 4-NT: 3.5 eV) and the electron affinity of NO_2 of 2.273 eV [26] the threshold energy for NO_2^- formation can be derived to be about 1.1 eV. Thermal excitation to this high energy is very unlikely and the only explanation of a zero energy peak is a complex rearrangement of the neutral products into more stable fragments like in the case of the 4 eV resonance of H^- (see above). The relative low abundance of the 0 eV peak and a weak unimolecular decay reaction from the excited parent anion into mass 46 support such a complex time consuming process. It is interesting to note that in contrast to the anion case, NO_2^+, however, is only very weakly formed upon electron impact ionization at electron energy of 70 eV [27]. Recently Havey et al. [12] using an apparatus with an electron energy resolution of ±300 meV [28] reported that the anion efficiency curves of the NO_2^- anion are characteristic for each isomer and suggested that this anion can be used to identify not only different nitroaromatic compounds but also even different isomeric forms. In a more extensive study including several other fragment anions Sulzer et al. [7] confirmed this finding but suggest for identification purposes to measure besides NO_2^- also $m/z=77$ and $m/z=88$. 4-NT is the only isomer that exhibits an intense resonance at electron energies higher than 6 eV for these two fragments.

The ion yield for $m/z=45$ (Fig. 4, lower diagram) is more than three orders of magnitude less intense than for the neighboring anion NO_2^-. All isomers show for this anion a resonance at 3.8 eV and only 2-NT shows an additional resonance at higher energies, i.e., at 8.8 eV. The most likely composition of this anion at low-energy resonance is CH_3NO^- and just for 2-NT the proximity between the methyl and the nitro group allows the formation of $HCOO^-$ at 8.8 eV. Collision induced dissociation experiments carried out for $m/z=45$ at 4 eV and 8.8 eV confirm this explanation. $m/z=42$ is the second highest intensity anion containing three heavy atoms. The ratio of the abundance of $m/z=43$ and $m/z=42$ is 1.5% which corresponds perfectly to what is expected for CNO^-.

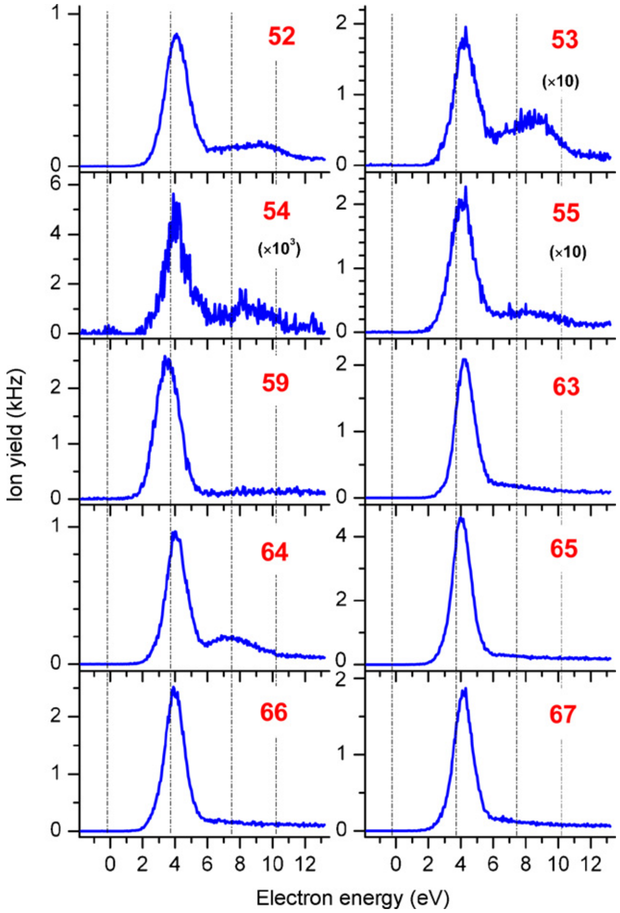

Fig. 7. Anion efficiency curves for the formation of anions with $m/z=52$ to $m/z=67$ upon dissociative electron attachment to 2-nitrotoluene. All anions were measured with the sector field mass spectrometer with an electron energy resolution of about 1 eV. The electron current was set to 10 μA and the pressure in the ion source was 2×10^{-4} Pa.

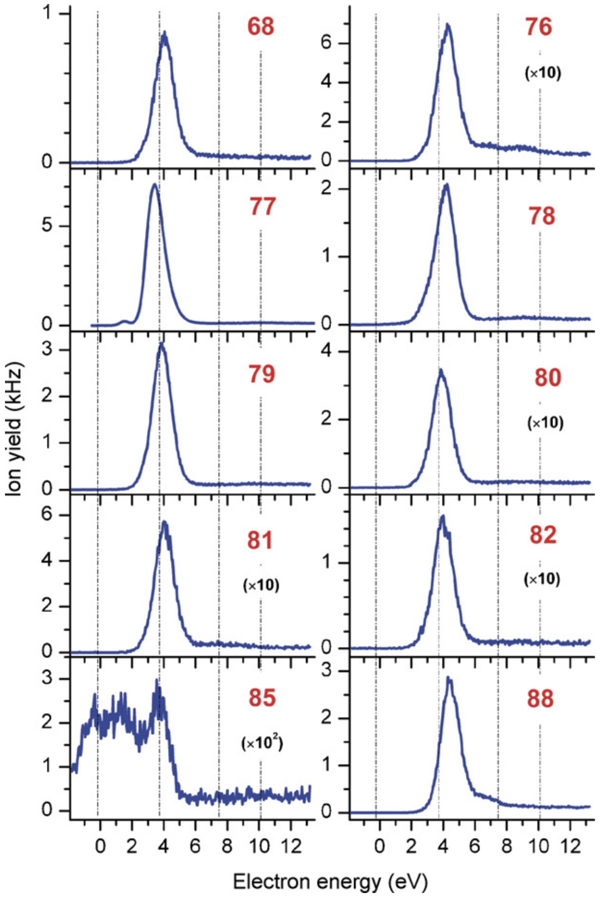

Fig. 8. Anion efficiency curves for the formation of anions with $m/z = 68$ to $m/z = 88$ upon dissociative electron attachment to 2-nitrotoluene. All anions were measured with the sector field mass spectrometer with an electron energy resolution of about 1 eV. The electron current was set to 10 µA and the pressure in the ion source was 2×10^{-4} Pa.

3.4. Four heavy atoms fragment anions (m/z = 49–59)

The dominant fragment anion of this group is $m/z = 52$. This anion can be assigned to $C_4H_4^-$. The similar height of all neighboring peaks and the average mass of this group also support only an insignificant contribution of nitrogen and oxygen to this group. The only exception is mass 59, which has to contain one or two oxygen atoms. The ion yield of the two next heavier masses (about 3% and 2%) of $m/z = 59$ suggest CH_3COO^- as the most likely structure of $m/z = 59$.

3.5. Five heavy atoms fragment anions (m/z = 63–68)

All anions of this group have ion yields below 10 kHz. However, there relative abundance is quite similar and the average mass of this group again suggest predominantly pure hydrocarbon fragments in this mass range. The most intense fragment is $m/z = 65$ which we assign to the fragment $C_5H_5^-$. It is about three orders of magnitude less intense than the NO_2^- anion. For electron impact ionization the same mass has also the highest yield in this mass range [27]. The relative abundance of $C_5H_5^+$ is 95% of the most intense cation that is formed upon electron impact ionization of 2-nitrotoluene with 70 eV electrons [27]. Mass $m/z = 64$ is the only fragment that shows a noticeable second resonance at an electron energy different to 4 eV.

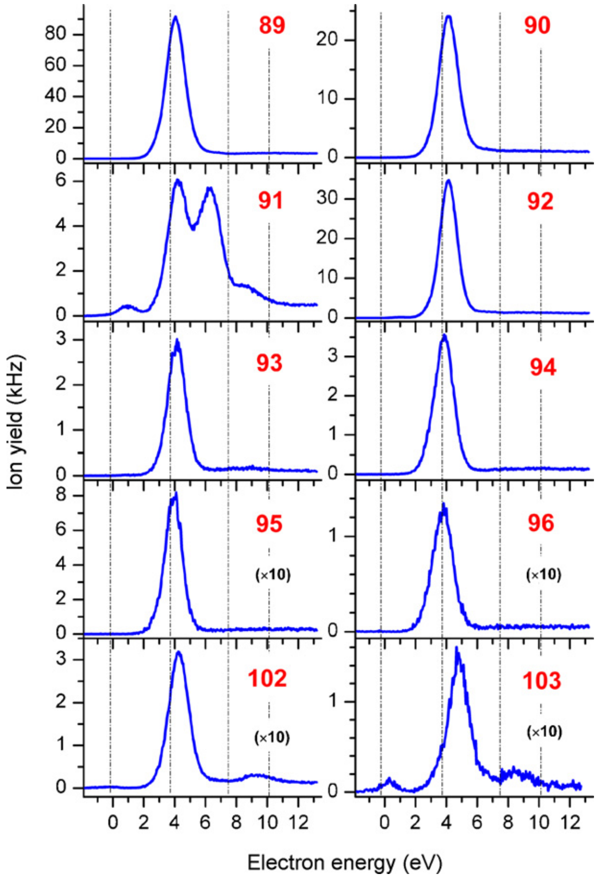

Fig. 9. Anion efficiency curves for the formation of anions with $m/z = 89$ to $m/z = 103$ upon dissociative electron attachment to 2-nitrotoluene. All anions were measured with the sector field mass spectrometer with an electron energy resolution of about 1 eV. The electron current was set to 10 µA and the pressure in the ion source was 2×10^{-4} Pa. The anion with $m/z = 91$ which we assign to the loss of neutral NO_2 was measured with the electron monochromator instrument with an electron energy resolution of 80 meV and the curve was normalized to the sector field data at the 4 eV resonance. For $m/z = 91$ only the anion efficiency curve measured with the monochromator instrument is shown.

3.6. Six heavy atoms fragment anions (m/z = 76–82)

Like in the case of five heavy atoms all fragment anions of this group of peaks have rather similar and low intensities. All anions predominantly are formed at 4 eV. The most abundant fragment is $m/z = 77$ which we assign to the fragment $C_6H_5^-$. The anion efficiency curve of this anion shows a weak resonance at 1.5 eV. Only eight other fragment anions reveal a resonance between 1 eV and 1.5 eV and all of them correspond to complete or partial loss of the NO_2 and/or CH_3 group. Again the corresponding cation $C_6H_5^+$ has the highest intensity in this mass range for positively charged ions formed upon electron impact ionization at 70 eV [27].

3.7. Seven heavy atoms fragment anions (m/z = 88–96)

Mass 89 has the highest abundance of this group and is the third most intense anion produced. Again the average mass of

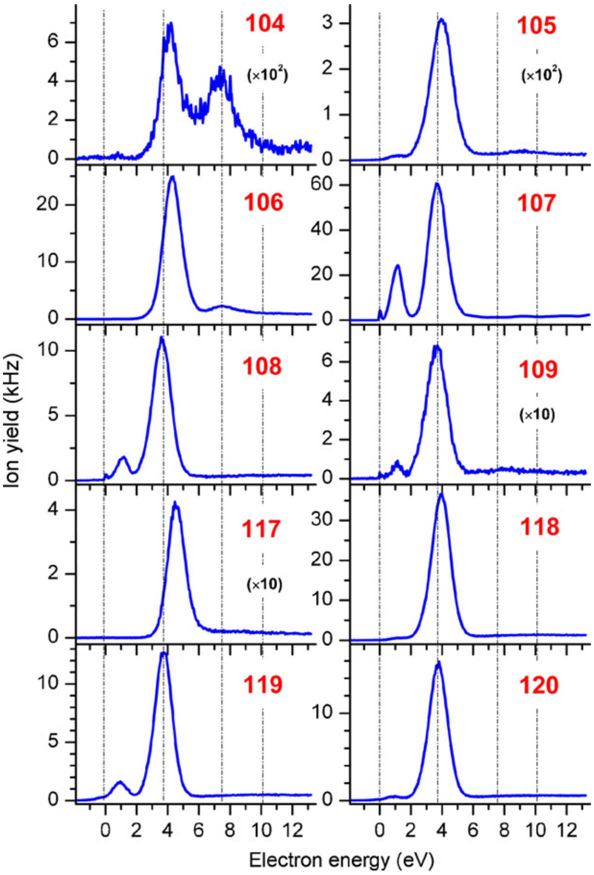

Fig. 10. Anion efficiency curves for the formation of anions with $m/z = 104$ to $m/z = 120$ upon dissociative electron attachment to 2-nitrotoluene. All anions were measured with the sector field mass spectrometer with an electron energy resolution of about 1 eV. The electron current was set to 10 μA and the pressure in the ion source was 2×10^{-4} Pa. The anions with $m/z = 107$, 108, 109, 118, 119 and 120 were measured with the electron monochromator instrument with an electron energy resolution of 80 meV and the data were normalized to the sector field data at the 4 eV resonances of the anions. Only the anion efficiency curves measured with the monochromator instrument are shown for these masses.

this fragment anion group matches perfectly with pure hydrocarbons and thus the loss of the NO_2 group. The positive ion mass spectrum shows the most intense peak at $m/z = 92$ [27] which in contrast requires the presence of at least one nitrogen or oxygen atom in this fragment. Although the anion with a mass of 91 Da which we assign to a simple C–N bond cleavage and the loss of NO_2 has quite low abundance, it shows a unique anion efficiency curve that consists of a superposition of all resonances except the one at zero eV. This benzyl anion $C_7H_7^-$ is formed by loss of NO_2 from the mono-nitrotoluenes and is the complementary anion to the NO_2^-. For all isomers at higher electron energies three maxima at about 4.2 eV (except for 2-NT, 4.4 eV), 6.6 eV and 8.6 eV are present in the ion efficiency curves. The relative abundance of the two most intense resonances of the ion yields is a characteristic for each isomer. $C_7H_7^-$ is about five times more intense for DEA to 2-nitrotoluene compared to the other two isomers. This can be explained by the C–N bond weakening theoretically calculated by Chen and Wu [16].

The ion yield for the anion ($m/z = 88$) produced via loss of H_2O and HNO shows a single broad structure at 4 eV with a long tail towards higher energies for 2-NT and 3-NT. However, in the case of 4-NT the 4 eV resonance is strongly suppressed and the anion efficiency curve is dominated by a broad resonance at 10 eV [7].

3.8. Eight heavy atoms fragment anions ($m/z = 102$–109)

For this group of fragments the yield for cations is surprisingly low; $m/z = 107$ is the most intense cation and has a yield of less than 1% of the dominant cation at $m/z = 120$. In contrast for negatively charged ions these fragments are quite abundant and the anion with $m/z = 107$ that is formed via loss of NO is the dominant fragment. The position of the resonance at 3.7 eV is common for all isomers. In the ion yield of 2-nitrotoluene two low energy resonances at 0 eV and 1.1 eV are clearly visible. In the case of 3-NT and 4-NT the 1.1 eV peak is about three orders of magnitude less intense and the 0 eV resonance does not appear at all in the anion efficiency curves. The low energy features of this anion are also visible for $m/z = 108$ and 109 and the ratios of the abundance fit nicely with the isotopic pattern of [M–NO]. In contrast at 4 eV the anion yield of $m/z = 108$ and 109 is substantially higher compared to the isotopic ratio and

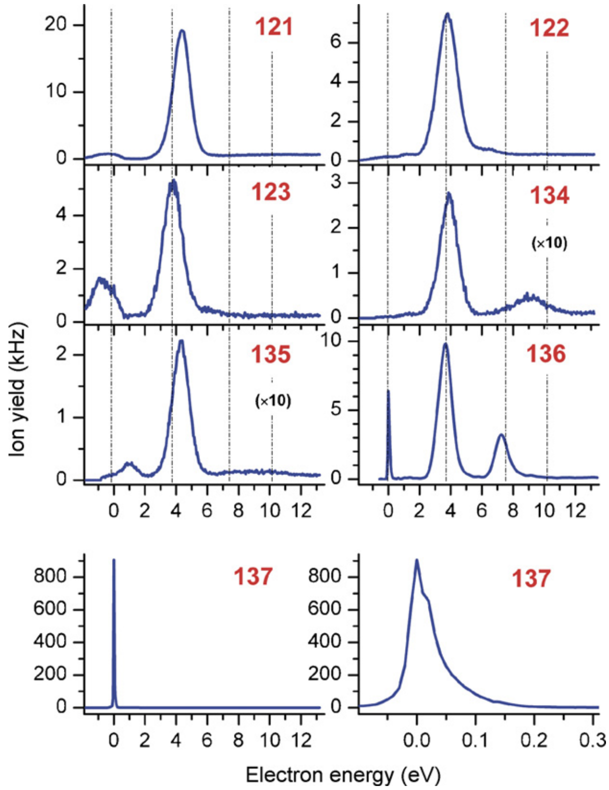

Fig. 11. Anion efficiency curves for the formation of anions with $m/z = 121$ to $m/z = 137$ upon electron attachment to 2-nitrotoluene. All anions were measured with the sector field mass spectrometer with an electron energy resolution of about 1 eV. The electron current was set to 10 μA and the pressure in the ion source was 2×10^{-4} Pa. The anions with $m/z = 122$, 136 and 137 were measured with the electron monochromator instrument with an electron energy resolution of 80 meV and the data were normalized to the sector field data at the 4 eV resonances of the fragment anions. Only the anion efficiency curves measured with the monochromator instrument are shown for these masses.

thus an additional fragment anion is contributing to the main resonance at these masses.

3.9. Nine heavy atoms fragment anions (m/z = 117–123)

The ions with $m/z = 120$ we associate with an ionic structure which is formed via loss of an OH radical. These ions are formed via a core-excited resonance at approximately 4 eV in all three isomers. The efficiency of $[M–OH]^-$ formation is largest for 4-NT (about 10 times more intense compared to the other two isomers). This could indicate that the hydrogen transfer from the toluene ring may play an important role in this reaction and that the hydrogen atoms from the methyl group are not involved in the formation of the OH radical. In the case of 2-NT the formation of $[M–OH]^-$ anion is additionally observed via a resonance at 1.1 eV. This resonance we attribute to the π^* resonance in NO_2. This core-excited resonance in 3- and 4-NT is shifted by 240 meV and 390 meV, respectively, towards higher energies in comparison to the corresponding peak in 2-NT. Evidently the distance between the nitro and the methyl group does not influence only the magnitude of the cross section but also the position of the resonance. The *sequential* emission of an oxygen and hydrogen atom and subsequent formation of the $[M–OH]^-$ anion requires a minimum energy of 9.2 eV. This value is calculated with high-level *ab initio* calculations using the G2MP2 [29] method with an uncertainty of about ±0.1 eV [29,30]. Thus we conclude that at least for all electron energies below 9.2 eV the neutral product has to be the OH radical.

The position and width of the resonances of $m/z = 119$ are almost identical to the OH loss discussed above. Again, only 2-NT shows a low energy resonance at 1.2 eV. The energetic situation for this reaction does not allow the loss of three neutral atomic fragments and thus we assign the formation of this anion via loss of a water molecule. Within the uncertainty of the experiment all isomers have its most abundant resonance at 3.75 eV for $[M–H_2O]^-$. The most abundant anion that is formed via loss of one heavy atom is $m/z = 118$. The only possible reaction is the loss of OH and H_2. This anion is exclusively formed via the resonance at about 4 eV.

3.10. Ten heavy atoms fragment anions (m/z = 134–139)

In many organic molecules closed shell negative ions are effectively formed via hydrogen loss:

$$e + M \rightarrow M^{\#-} \rightarrow [M–H]^- + H \tag{4}$$

For DNA bases [31,32] and organic acids [33] this reaction leads to the dominant negatively charged product and furthermore, in several cases this reaction shows a remarkable site selectivity as a function of the kinetic energy of the attaching electron [20,21,34]. Reaction (4) is also observed here for DEA to the mono-nitrotoluenes. The ion efficiency curves for $[M–H]^-$ exhibit for all isomers several resonances with maxima at about 0 eV, 3.7 eV, 7.15 eV and 8 eV. Whereas the positions of all these resonances agree rather well for all isomers, the relative intensities are quite different. The narrow resonance close to zero is about two orders of magnitude more intense for 2-NT compared to the other isomers. 4-NT, however, shows much higher intensity for the high-energy resonances and even shows a clear structure at 10 eV that is completely missing for 2-NT and 3-NT. The non-zero eV peaks could be associated with the first, second and third core-excited resonance of mono-nitrotoluenes and the relative intensities of the resonances are characteristic for particular isomers of mono-nitrotoluene. Similar resonances (with respect to the positions of the observed peaks) were also observed for nitrobenzene [35].

In concluding, by analyzing the position of all resonances of 77 fragment anions formed upon DEA to 2-nitrotoluene and comparing them with the anion efficiency curves of corresponding product anions of 3- and 4-nitrotoluene and nitrobenzene taken from the literature [6] the following general trends are observed:

(i) For an electron energy above 2 eV the ion yields of fragment anions of mono-nitrotoluene show exceptionally low lying core excited resonances with a maximum at about 4 eV. At this electron energy even low mass fragments such as H^- and C^- are present. These anions can only be formed via a complex rearrangement of the neutral fragments into substantially more stable products.

(ii) Additional high-energy resonances are observed at 6.5 eV, 7.5 eV and 10 eV that decrease in intensity with the proximity between the methyl and the nitro group. For DEA to nitrobenzene, only one additional high-energy resonance at about 7 eV was observed [6,35]. At 10 eV typically H^- is formed upon DEA to hydrocarbon molecules. However, in the present case this resonance cannot be observed for this anion. However, several other fragment anions such as CH_2^- and C_2H^- are formed at this electron energy.

(iii) The total anion efficiency curves for the three isomers are dominated by the NO_2^- and parent anion and reveal pronounced differences between each other. With increasing distance between the two functional groups, i.e., NO_2 and CH_3, the low energy features decrease in intensity. For NO_2^- formed upon DEA to 2-NT and 3-NT a similar observation was reported by Christophorou et al. [11].

The present study shows that electron attachment to nitroaromatic compounds leads to mass spectra that contain almost as many product ions as positive mass spectra formed upon electron impact ionization at 70 eV. Such a rich fragmentation can only be explained by complete randomization of the initially deposited electronic excitation energy into the vibrational degrees of freedom. However, the relative abundance of corresponding mass groups for cations and anions can differ up to three orders of magnitude. For mono-nitrotoluene the competition of fragmentation into so many products starts with the 4 eV resonance. For di- and even more for the trinitrotoluene this massive fragmentation is even observed at zero eV [36]

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