Dissociative electron attachment to nitroaromatic compounds – resonances as fingerprints for isomers

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Abstract. We present detailed free electron attachment measurements on nitroaromatic compounds in the gas phase. It turns out that dissociative electron attachment can act as a selective and sensitive probe for the identification of isomeric forms of nitrotoluene and dinitrobenzene. Rich fragmentation patterns have been observed for both nitroaromates and all fragments above the detection limit of our instrument have been investigated with a high energy resolution electron monochromator in the energy range of about 0 to 15 eV. It is shown that relative attachment cross section curves can act as fingerprints for the particular molecule and its isomers. Additionally it has been observed that numerous fragments arise from surprisingly complex structural and electronic rearrangements.

1. Introduction

Nitroaromatic compounds are being widely used in industrial processes, especially in their function as explosives or additives to explosives [1]. One of the best known nitroaromate is trinitrotoluene (TNT) which is still used as a measure of the explosive power of modern explosives. Therefore a reliable and effective detection method for these substances is desirable. However mass spectrometric detection attempts via electron impact ionization have the disadvantage of producing a multitude of fragments, that makes an unambiguous identification a nearly impossible task. Notably, isomers often show more or less the same fragmentation patterns and are therefore not distinguishable by this method. In contrast, dissociative electron attachment (DEA) is a resonant process where the electron energy acts as an additional information for identification [2]. It even turns out that isomers have different attachment resonances and can therefore easily be distinguished [3].

In the present study we concentrate on the relative attachment cross sections (so called energy spectra) of nitrotoluene (NT) and dinitrobenzene (DNB) isomers (2-, 3- and 4-NT resp. 1,2-, 1,3- and 1,4-DNB) as a function of the incident electron energy. Studies using electron beam and swarm...
techniques have been performed rather early [4-9], where mainly the formation of NO$_2^-$ and the unusual long lifetime (µs to ms range) of the molecular anions were investigated. Other studies considered the potential of NO$_2^-$ to act as a fingerprint for the identification of the neutral compound [10-12]. In contrast to these former studies, our measurements stand out not only because of the high electron energy resolution achieved (i.e., 60 meV) and large signal/noise ratios but also because of the investigation of various additional fragments.

2. Experimental setup
The present measurements have been carried out utilizing a crossed electron/molecule beam device that has been described in detail previously [13].

![Figure 1. Schematics of the experimental setup](image)

The electron beam, emitted by a hairpin filament, passes a custom built hemispherical electric field sector, which reduces the energy spread down to 50-100 meV at an electron current of 5-20 nA. In the collision chamber the monochromatized electron beam perpendicularly crosses the molecular beam. No further extraction field is applied to guide the produced anions into a quadrupole mass filter, where the anions are separated by their mass to charge ratio (m/z). A channeltron type secondary electron multiplier operated in single pulse count mode is used as a detector. For a schematic overview of the experimental setup, see Figure 1.

Depending on the vapor pressure of the substance under study, the sample is either filled into an oven inside the vacuum chamber, where it is slightly heated (around 50° C), or directly introduced via a gas inlet system. In both cases the molecular beam is guided to the collision chamber by a thin capillary to produce an effusive beam. All samples are commercially available and have been bought from Sigma-Aldrich with a stated purity of approximately 99 %.

The energy scale is calibrated by measuring the well known Cl'/CCl$_4$ respectively SF$_6$/SF$_6$ signal around 0 eV electron energy, which allows to determine the energy resolution and calibrate the energy scale. In the past we experienced that under certain conditions the presence of CCl$_4$ as a background gas can lead to "trojan horse ionization" [14] at 0 eV electron energy. All 0 eV peaks in the present work have been carefully checked with and without the presence of CCl$_4$ and therefore artifacts of this kind can be excluded.

3. Results
In Figures 2 and 3 negative ion mass spectra for all NT and DNB isomers are shown. For NT the spectra are taken at an electron energy of 4 eV as most fragments have at least one resonance at this
energy. The spectra for DNB are taken from about 0 to 10 eV in 1 eV steps and summed up as there is no common energy where all fragments would be visible. Due to the large number of fragments for NT and DNB it seems obvious that complex structural rearrangements occur.

In Table 1 the most abundant fragments are identified. For DNB these identifications have been proven by investigating three variations of DNB that are commercially available from Sigma-Aldrich: a) all H atoms replaced by D, b) all C atoms replaced by $^{13}$C and c) both N atoms replaced by $^{15}$N. As it turned out, that the replacement of C or N atoms by their isotopes makes no measurable differences in the energy spectra, the fragments could be easily identified and compared. The compositions were then calculated via the mass difference of the fragments that were formed in "regular" DNB and in the DNB containing the isotopes.

![Figure 2. Negative ion mass spectra at 4 eV for 2-, 3- and 4-NT](image)

![Figure 3. Negative ion mass spectra summed up from about 0 to 10 eV in 1 eV steps for 1,2-, 1,3- and 1,4-DNB](image)

All NT and DNB isomers show 0 eV resonances for the parent anion (m/z=137 for NT and 168 for DNB). Especially for 1,3-DNB a clearly separated second peak below 0.5eV is visible, which is not the case for the nitrotoluenes (Figures 5 and 6).

![Figure 4. Chemical structures of 2-, 3- and 4-NT (for DNB the methyl-group is replaced by an additional nitro-group)](image)
The abstraction of neutral H, O and NO$_2$ is expected if one looks at the chemical structures (Figure 4). In contrast the presence of m/z=107 for NT resp. m/z=138 for DNB seems very surprising as it originates from the abstraction of neutral NO whereas the leftover O atom of the nitro group remains at the molecule (most likely it forms a bond to one of the hydrogens of the benzene ring).

If we take a closer look at the energy spectra of the NT isomers, it turns out that 2SNT is easily distinguishable from the other two isomers (Figure 5). We attribute this to the fact that for 2-NT the steric distance between the methyl- and the nitro-group is the smallest and therefore conclude that this distance is mainly responsible for the differences in the spectra. According to calculations by Chen and Wu [15] this effect leads to a torsional angle of 22° for the nitro-group in 2-NT. The NO$_2$ yield (m/z=46) is a very good example to underline this steric theory, as the ratio between the peaks at ~1 and ~4 eV changes dramatically if we go from 2- to 3- or 4-NT. Between 3- and 4-NT this effect is much smaller, but still measurable. The opposite channel, namely the loss of a neutral NO$_2$ (m/z=91) shows this development even clearer. Again the 2-NT differs most by even exhibiting an additional peak between 1 and 2 eV. The peak at ~4 eV decreases as the distance between the methyl- and the nitro-group increases. All isomers are easily separable by just measuring the energy scan of this fragment, which demonstrates that these measurements may be used as a fingerprinting detection method as mentioned in the introduction.

For m/z=107, namely the NO loss, only the 2-NT differs from the other two isomers by having an additional peak around 1 eV.

It has to be noted, that all shown energy spectra are normalized to one characteristic peak (e.g. the 4 eV peak at m/z=46) as the apparatus does not allow the measurement of absolute cross sections. Therefore only the positions and the peak-ratios of the isomers are comparable, which is the fundamental idea behind a fingerprinting method.

The dinitrobenzene isomers are even easier distinguishable by their energy spectra (Figure 6). Here the spatial distance between the two nitro-groups seems to have the greatest influence on the relative cross sections. For the 1,2-DNB, where the two NO$_2$-groups are neighbouring, an additional peak around 1 eV for the NO$_2$ appears, that is missing for the other two isomers. Even more interesting is the region between 3 and 5 eV as there seems to be a superposition of two overlapping peaks. A multiple Gaussian fit in this region shows that the positions of these two peaks don't change and therefore that the apparent energy shift is only a product of different heights.

For the opposite channel, namely the abstraction of neutral NO$_2$ at m/z=122, again a systematic development is visible. It seems as if all peaks are shifted to higher energies with the distance of the nitro-groups increasing and as not only the ratios but also the positions of the peaks change significantly, this fragment is perfectly suited for an unambiguous isomer identification.

M/z=138, which we assign to neutral NO loss, also shows a very complex overlapping of various peaks. 1,3-DNB is the only isomer that shows nearly no contribution in the ~0 eV range. 1,2- and 1,4-

| Table 1. Identification of the most abundant fragments |
|------------------------------------------------------|
| Nitrotoluene | Dinitrobenzene |
| Mass | Identification | Mass | Identification |
| 137 | C$_7$H$_7$NO$_2$ | 168 | C$_6$H$_6$N$_2$O$_4$ |
| 136 | C$_7$H$_6$NO$_2$ | 167 | C$_6$H$_5$N$_2$O$_4$ |
| 120 | C$_7$H$_6$NO | 152 | C$_6$H$_5$N$_2$O$_3$ |
| 107 | C$_7$H$_5$O | 138 | C$_6$H$_5$NO$_2$ |
| 106 | C$_7$H$_6$O | 137 | C$_6$H$_5$NO$_3$ |
| 91 | C$_7$H$_7$ | 122 | C$_6$H$_6$N$_2$O$_2$ |
| 89 | C$_7$H$_6$ | 108 | C$_6$H$_5$O$_2$ |
| 46 | NO$_2$ | 92 | C$_6$H$_6$O |
|        | 46 | NO$_2$ |
DNB both yield two peaks in this region, whereas for 1,2-DNB these peaks are clearly separable and for 1,4-DNB they are closer to each other, so that the first peak diminishes to a shoulder on the left slope.

Dinitrobenzene is the only nitroaromatic compound we measured so far, where a difference in the energy spectrum for different isomers is even visible for the unfragmented parent anion. On m/z=168 only the 1,2-DNB shows a single 0 eV resonance with probably a small contribution of an additional peak on the right slope. In 1,4-DNB this assumed second peak develops to a distinct shoulder whereas 1,3-DNB breaks ranks by yielding a clearly separated peak between 0.2 and 0.4 eV that is not existing for the other two isomers.

4. Conclusion
We showed that dissociative electron attachment is a powerful tool not only to identify different molecules, but also the isomers of these molecules.

For nitrotoluene it is very easy to distinguish between 2-NT and the other two isomers in all fragment energy spectra. To separate 3- and 4-NT the fragment that remains after the loss of a neutral NO$_2$ seems to be the most suitable candidate.

For dinitrobenzene this separation is possible for all presented fragments and even, with limitations, for the parent anion.
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