



Interactions of multiple reactant ions with 2,4,6-trinitrotoluene studied by corona discharge ion mobility-mass spectrometry



Martin Sabo^{a,*}, Bartosz Michalczuk^b, Zuzana Lichvanová^a, Vladimír Kavický^c,
Branislav Radjenovic^d, Štefan Matejčík^a

^a Comenius University in Bratislava, Faculty of Mathematics, Physics and Informatics, Department of Experimental Physics, Mlynská dolina, F2 842 48, Bratislava, Slovakia

^b Siedlce University, Department of Chemistry, 3 Maja 54, 08110 Siedlce, Poland

^c University of Žilina, Faculty of Security Engineering, Department of Security Management, Univerzitná 8215/1, 010 26 Žilina, Slovakia

^d Institute of Physics, University of Belgrade, Belgrade, Serbia

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ABSTRACT

In this work we present a study of the interactions of multiple reactant ions (RI) generated in corona discharge (CD) with molecules of 2,4,6-trinitrotoluene (TNT) using the ion mobility orthogonal-acceleration time of flight mass spectrometry (IMS-*oa*TOF) technique. We have studied response of TNT molecules to different reactant ions (RI) such as O_2^- , Cl^- , $N_2O_2^-$, NO_3^- or $NO_3^-(HNO_3)$. The response of TNT to RI results in formation of multitude of species, such as TNT^- , $(TNT-H)^-$ and cluster ions. Additionally, we have investigated the stability of TNT^- ions as function of IMS gas temperature and drift field intensity and their conversion to $(TNT-H)^-$. Formation of some product ions was assigned to degradation of TNT by neutral reactive species generated by the CD.

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1. Introduction

The detection of explosives is an important task in order to ensure the security of the citizens around the world. The ion mobility spectrometer (IMS) is an instrument used in the security area [1,2], due to its compact design, fast response and ability to operate at atmospheric pressure. IMS is an ion separation technique based on the interactions of the ions with molecules of a buffer gas in weak homogeneous electric field. The gradual expansion of this technique was closely related with development and implementation of new ionisation sources for IMS instruments.

Most conventional ion source used in IMS is the radioactive ^{63}Ni due to its low noise, easy implementation, high reliability and long life time [1]. Main drawback of this source is its radioactivity and the restriction related to it in civil sector. Several non-radioactive ion sources were developed for explosives detection with IMS, such as electro spray ionisation (ESI) [3], secondary electro spray ionisation (SESI) [4], low temperature plasma ionisation (LTPI) [5], distributed

plasma ionisation (DPI) [6], dopant assisted photo ionisation (DAPI) [7,8] and corona discharge (CD) [9,10].

The CD ionisation source implemented to IMS attracted attention as a nonradioactive alternative to ^{63}Ni . The main drawback of CD source is the need of additional high voltage power supply. This deficiency is on the other hand strongly compensated by its significantly higher signal yield. The major advantage of this ionisation source is its ability to selectively generate different reactant ions (RI).

Different RI allow application of different chemical ionisation schemes for given analyte, which result in different product ions and the sensitivity and selectivity of IMS technique can dramatically increase with properly chosen RI. In the positive polarity, the CD ion source in air is able to selectively generate $H_3O^+(H_2O)_n$ or $NO^+(H_2O)_n$ RI [11]. The $NO^+(H_2O)_n$ reactant ions significantly increase the sensitivity of IMS instrument for detection of monoaromatic compounds. In the negative polarity, used for explosives detection, the situation is more complicated. This is related to neutrals and radicals generated in CD in air and their fast conversion to very stable negative ions (high electron affinity) such as NO_3^- , $N_2O_2^-$, O_3^- , CO_3^- , $NO_3^-(HNO_3)$ and many others [12–16]. The yield of specific species strongly depends on the parameters of CD, the geometry, gas flow, gas purity, discharge power and temperature. The deployment of reverse gas flow (gas flow is opposite to ions

* Corresponding author. Tel.: +421260295686.

E-mail address: matejcik@fmph.uniba.sk (M. Sabo).

movement in CD gap) also allows the generation of “soft” RI as O_2^- and CO_4^- [17,18].

In spite of the fact that CD was implemented to IMS nearly fifteen years ago [9], only a few works deal with implementation of this ionisation source to explosives detection. Tabrizchi and Ilbeigi implemented CD operated in positive polarity for explosives detection [19]. In the negative polarity, Tabrizchi and Abedi [20] proposed a curtain gas CD design. This technique has notable sensitivity [21], however the non-attaching gas is required. Another CD-IMS work supported also by MS instrument used mainly NO_3^- and $NO_3^- \cdot HNO_3$ RI, respectively [22–24] for explosives detection.

In this work, we will carefully investigate the reactions of multiple RI such as $N_2O_2^-$, NO_3^- , $NO_3^- \cdot HNO_3$, $NO_2^- \cdot HNO_3$, O_2^- and Cl^- with the most common explosive 2,4,6-trinitrotoluene (TNT) by the CD-IMS-oaTOFMS instrument. In order to explore possible product ions and their stability, we have investigated the influence of IMS gas temperature, drift field intensity, discharge power, gas flow and TNT concentration.

2. Experiment

2.1. IMS-oaTOFMS instrument

The IMS interfaced to oaTOFMS instrument was described in detail in [13,11]. In the present study, the IMS was operated at atmospheric pressure and in the gas temperature range from 305 to 363 K. The length of the drift tube was 8.25 cm and the intensity of the IMS electric field was 495 V cm^{-1} (if not stated other). In the case of the stability study of the product ions we have varied the drift field intensity from 350 to 543 V cm^{-1} . The Bradbury-Nielsen type of shutter grid (SG) was operated with pulse width 110 μs and frequency 50 Hz. The ionisation source was CD in point to plane geometry. The point electrode was manufactured with tungsten wire of 100 μm diameter and located 5 mm from the plane electrode. The discharge power of CD was varied in the range from 10 to 50 μA in order to control the nature of RI ions [13,25]. The IMS instrument was operated only in negative polarity. The tandem IMS-oaTOFMS instrument was operated in three analytical modes. In the “IMS mode” only the IMS instrument was used, in the “TOF mode” (IMS gate open) with MS analysis and in the two dimensional “IMS-MS mode” (synchronised operation of IMS and MS) resulted in the 2D IMS-MS maps. The operation parameters of our IMS-oaTOFMS instrument are listed in Table 1.

2.2. The corona discharge modes of operation and reactant ions

Two basic operation modes of CD IMS are schematically illustrated in Fig. 1. Fig. 1a shows the gas outlet of IMS instrument located behind the corona discharge. In this case, direction of the gas flow is opposite to the direction of ions movement in the

discharge gap. This kind of CD gas flow was called as “the reverse gas flow mode”. On the other hand in Fig. 1b we can see the gas outlet of IMS instrument located in the reaction region of IMS and the gas flow follows the direction of the ions in CD gap. This gas flow mode was called as “standard gas flow mode”.

2.2.1. Reverse gas flow mode – $O_2^-(H_2O)_n$ and Cl^- reactant ions

In the reverse gas flow (Fig. 1a) the neutrals and radicals formed in CD are removed from reaction region of IMS and the high energetic electrons in CD gap are thermalised [17]. Due to these two effects the generation of “soft” RI, such as $O_2^-(H_2O)_n$ are formed and survive. In this mode we have worked with zero air at 1 L/min flow rate. The soft reactant ions allow charged transfer ionisation of analytes and in the case of carbon tetrachloride admixture (20 ppm of CCl_4 – dopant gas) formation of Cl^- reactant ions [26].

2.2.2. Standard gas flow mode – $N_2O_2^-$, NO_3^- , $NO_3^- \cdot HNO_3$, $NO_2^- \cdot HNO_3$ reactant ions

In standard gas flow mode the neutrals and radicals like O_3 and NO_x are moved in the same direction as the movement of primary ions. This results in formation of species like $N_2O_2^-$, NO_3^- , $NO_3^- \cdot HNO_3$ and $NO_2^- \cdot HNO_3$ in CD gap. In the standard flow regime (Fig. 1b) we modify the composition of the RI by variation of CD current. If the CD is operating in “low power mode” (CD current 10 μA), the main RI are $N_2O_2^-$, NO_3^- , $NO_3^- \cdot HNO_3$ and $NO_2^- \cdot HNO_3$ [13]. At “high power mode”, (discharge current 50 μA) $NO_3^- \cdot HNO_3$ RI dominates [13]. The CD gas flow was 0.2 L/min and the IMS drift gas flow was 1 L/min (all gasses zero air).

2.3. Gases and chemicals

The high purity N_2 and O_2 (purity 99.999%) were used in this experiment and their mixture in the ratio 4:1 was used as a zero air. The zero air was used as a drift as well as a CD gas in standard gas flow mode. The TNT was obtained from Slovak Department of Defense with purity up to 99%. The carbon tetrachloride of purity 99% was used as a dopant.

2.4. Sample preparation

The TNT sample was introduced to the reaction region of IMS by evaporation. The 5 mg of TNT located in aluminium container was evaporated using a heater made of micron wire and mica plates [27]. The evaporation temperature was controlled in the range from 308 to 453 K. The zero air with flow rate of 50 mL/min, transported the TNT vapours into the reaction region of CD-IMS-oaTOF instrument. For the calculation of TNT concentration we used known vapour pressure values of TNT as function of temperature [28]. The concentration was calculated for the volume of 50 mL what was the volume of the gas that flows around the heated sample in 1 min. As the gas flow was relatively low, we believe that the TNT vapours reached the saturated equilibrium. As this study was not quantitative in terms of detection limits, we found this method sufficient.

3. Results and discussion

The present results are presented in two sections according to the RI applied. In the first section we are going to discuss the product ions of TNT generated in interaction of RI formed in “reverse gas flow mode”, while the second section discusses the product species observed when the CD was operating in “standard gas flow mode”.

Table 1
Operation parameters of CD-IMS-oaTOFMS instrument.

| | |
|--------------------------|-------------------------------------|
| IMS | |
| Drift tube length | 8.25 cm |
| Electric field intensity | $350\text{--}543 \text{ V cm}^{-1}$ |
| SG pulse | 110 μs |
| Drift gas flow | 1 L/min |
| Sample gas flow | 50 mL/min |
| CD-gas flow | 0.2 L/min |
| Drift tube temperature | 305–363 K |
| Used resolution | ≈ 30 |
| CD current | 10–50 μA |
| oaTOFMS | |
| TOF pulse width | 10 μs |
| TOF pulse frequency | 40 kHz |
| TOF acceleration voltage | 2185 V |

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