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Title of primary article: **Desorption Electrospray Ionization of Explosives on Surfaces: Sensitivity and Selectivity Enhancement by Reactive Desorption Electrospray Ionization**

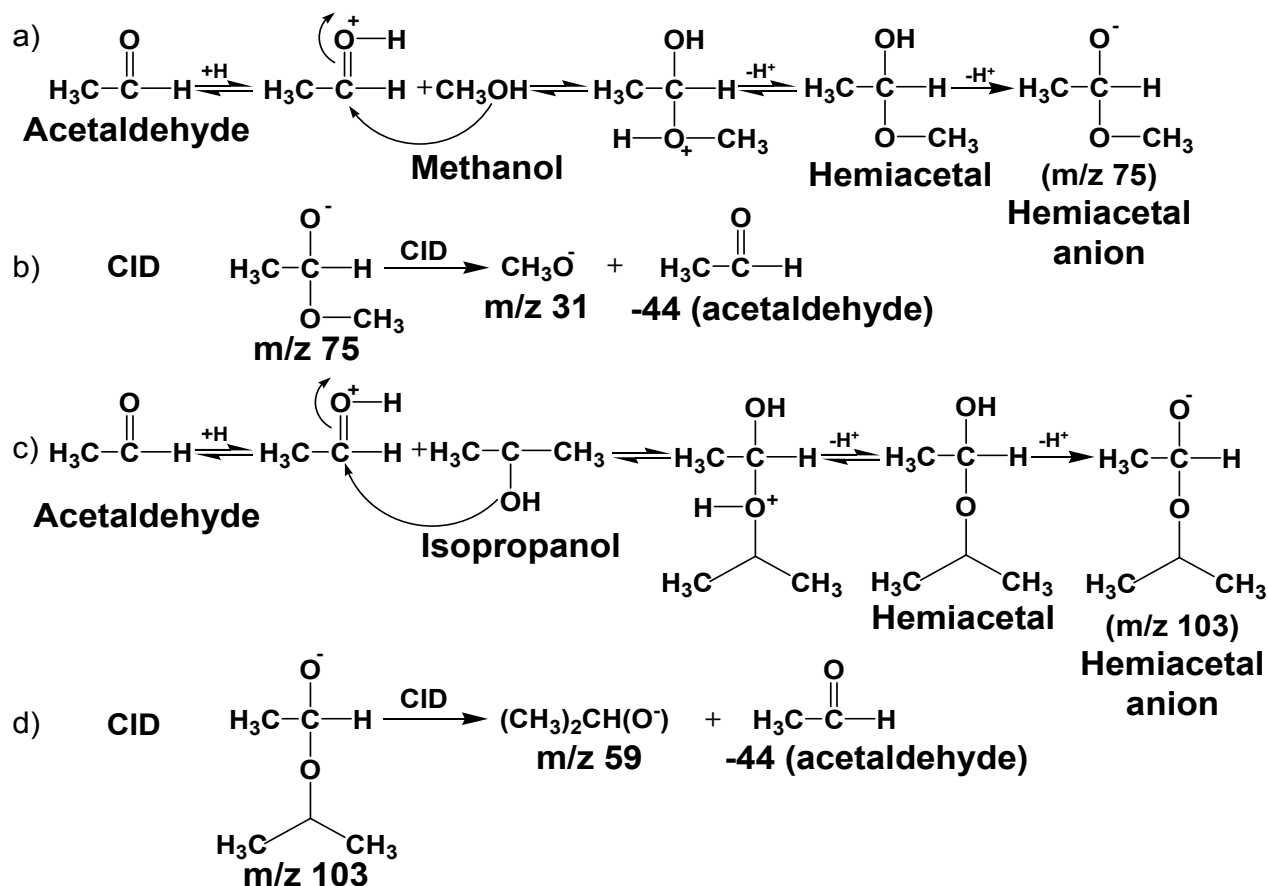
Abstract: Additional information is presented regarding the nature of the RDX adduct ions at m/z 297 and m/z 519, formed by addition of an ion of m/z 75 to one and two molecules of RDX, respectively.

The negatively-charged ions at m/z 297 and m/z 519 are adducts of RDX with an anion of mass 75. They have been previously studied by several groups¹⁻³ using ESI with disagreement as to their nature. The composition of the anion $C_2H_3O_3$ has been reported but exact mass information is not cited in the original paper.¹ This ESI Fourier transform ion cyclotron resonance study suggested formation of an RDX adduct with a formate anion $(HCO_2)^-$ plus one formaldehyde (H_2CO) molecule probably arising from impurities in the acetonitrile/0.5% ammonium hydroxide (NH_4OH) solvent used to prepare the RDX sample solutions.¹ Subsequently, an ESI liquid chromatography experiment performed using a triple quadrupole mass spectrometer led to the suggestion that the composition of the ion at m/z 297 was $(RDX + NO_2 + CH_3O - 2H)^-$ when a methanol/water (1:1) solution of RDX was used as solvent and mobile phase.² In yet another recent study, using ESI liquid chromatography mass spectrometry (ESI LC/MS) performed using an ion trap mass spectrometer and methanol/water (1:1) as solvent and mobile phase, the ion at m/z 297 was assigned as an adduct of RDX with a glycolic acid anion $(CH_2(OH)COO)^-$ present in methanol as an impurity at an estimated upper limit of 8 ppm.³ Note that the composition of this anion, $C_3H_7O_2$, is not in agreement with that $C_2H_3O_3$ reported in ref. 1.

In this study we show that, at least in the case of DESI, the $(M + 75)^-$ and $(2M + 75)^-$ adducts, at m/z 297 and m/z 519, are due to complexation of RDX with a hemiacetal $[(CH_3O)CH(CH_3)O]^-$ anion, which is itself the product of reaction between acetaldehyde and methanol (Scheme S-1). Acetaldehyde is present in methanol as an impurity at an upper level of 0.001 % (10 ppm), as determined by the manufacturer. The resulting hemiacetal is present as an anion at m/z 75 in all background spectra from all surfaces examined when a methanol/water spray solution is used with or without additives. In an experiment in which the spray solvent was directed into the transfer capillary of the mass spectrometer and an ESI spectrum was recorded, the hemiacetal anion was seen at m/z 75. When spraying only water into the mass spectrometer no signal at m/z 75 was observed. When the same experiment was repeated using pure methanol as spray solvent, the ion at m/z 75 was present in the mass spectrum. These experiments indicate that the ion at m/z 75 does not come from RDX fragments, products of RDX decomposition, water, or from the surface.

The composition of the hemiacetal anion at m/z 75 was assigned by tandem MS, using deuterated forms (CD_3OD , CD_3CDO) of methanol and acetaldehyde and by noting the formation of a homologous hemiacetal by

reacting isopropanol instead of using methanol with acetaldehyde. Tandem MS showed that the hemiacetal anion of m/z 75 loses an acetaldehyde molecule (-44) when either undeuterated or deuterated methanol is used, giving



Scheme S-1 Hemiacetal formation mechanism in the reaction between (a) methanol and (c) isopropanol with acetaldehyde giving products ions at m/z 75 and m/z 103, respectively. Collision-induced dissociation (CID) fragmentation mechanisms are shown for (b) the hemiacetal anion of m/z 75 and (d) the hemiacetal anion of m/z 103.

product ions at m/z 31 and m/z 34 corresponding to CH_3O^- and CD_3O^- , respectively (Scheme 1b). In a separate experiment performed using deuterated acetaldehyde, a loss of deuterated acetaldehyde (-48) was observed giving a product ion at m/z 31, corresponding to CH_3O^- .

These isotopic labeling experiments were repeated for 1ng RDX samples deposited on 1 cm^2 of paper in order to confirm that the increments in mass of 75 units for the ions at m/z 297 and m/z 519 were indeed due to adducts of the hemiacetal anion with one and two RDX molecules, respectively. Three ion pairs were observed at m/z 75/78, m/z 297/300, and at m/z 519/522 when a methanol/methanol- d_4 /water (1:1:1) solution was used as

spray solvent (Figure S-1a). These ion pairs correspond to the undeuterated and deuterated hemiacetal anions (m/z 75/78) and to their adducts with one (m/z 297/300) and two (m/z 519/522) RDX molecules. The same experiment was performed using deuterated acetaldehyde (CD_3CDO) and it showed a shift of 4 mass units for the hemiacetal anion at m/z 75 and for the adduct ions. The product ion MS/MS spectra of m/z 297 and m/z 300 showed the loss of the undeuterated (-76) and deuterated (-79) hemiacetal giving a product at m/z 221 corresponding to deprotonated RDX. The ions at m/z 519 and m/z 522 showed the loss of one RDX molecule, with product ions at m/z 297 and m/z 300 corresponding to RDX adducted with the undeuterated and deuterated forms of the hemiacetal.

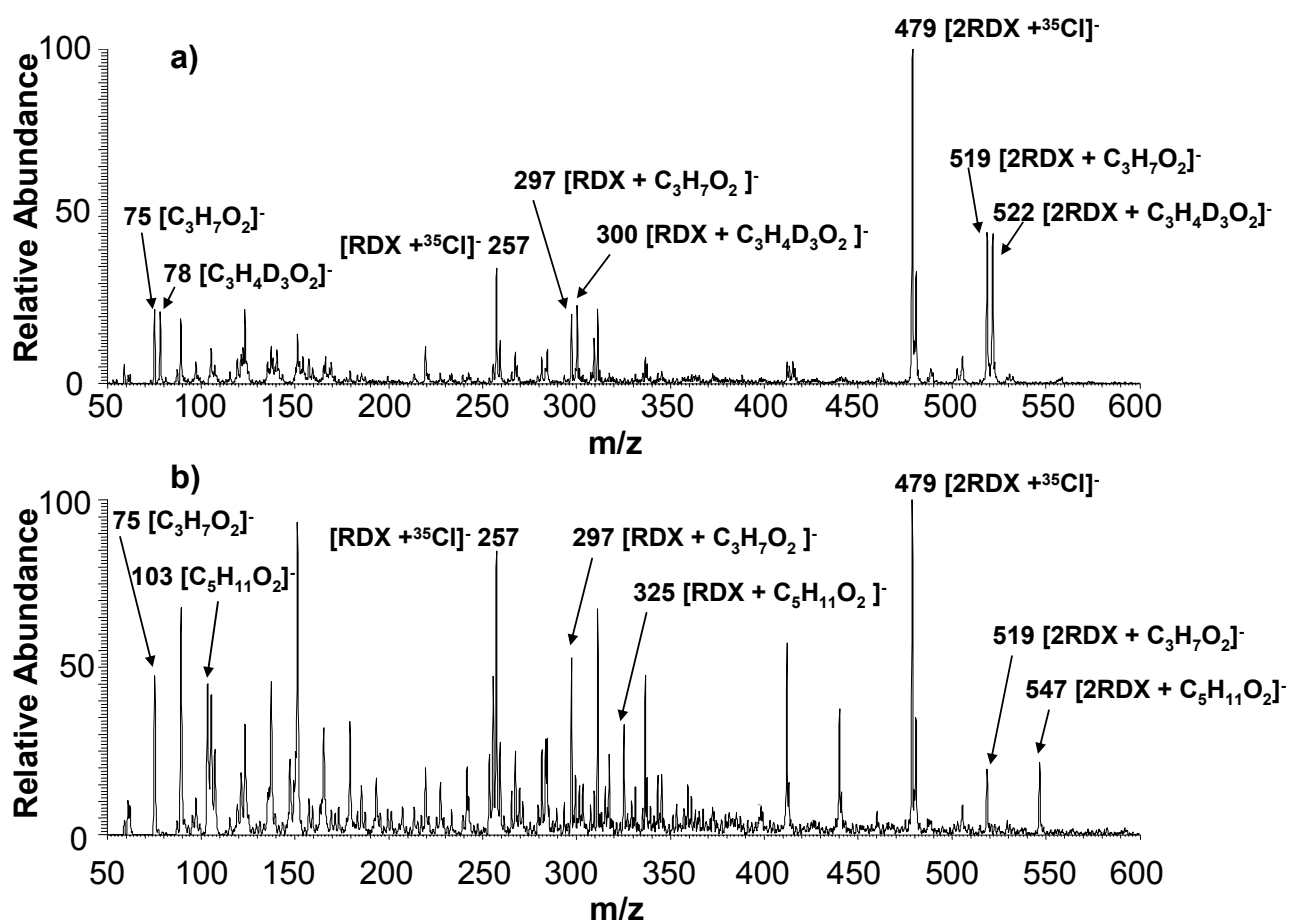


Figure S-1 Negative ion DESI mass spectrum of 1 ng RDX total amount deposited on paper in a total area of 1 cm^2 using as spray solvent a solution of (a) methanol/methanol- d_4 /water and (b) methanol/isopropanol/water, showing three ions pairs corresponding to the deuterated and undeuterated hemiacetal anions and their adducts with one and two RDX molecules, respectively.

In another experiment done to confirm the composition of the hemiacetal anion at m/z 75 and the adduct formation mechanism giving rise to the ions at m/z 297 and m/z 519, a solution composed of isopropanol/methanol/water (1:1:1) was used as the spray solvent. Isopropanol was used as an alternative to methanol and it reacted with acetaldehyde to form another hemiacetal anion at m/z 103 ($C_5H_{11}O_2^-$) while the original hemiacetal formed from methanol was still present at m/z 75 (Figure S-1b). The mechanism of formation and CID dissociation of the hemiacetal anion at m/z 103 is shown in schemes S-1c and S-1d, respectively. Figure S-1 b shows three ion pairs at m/z 75/103, m/z 297/325 and m/z 519/547 as expected for the hemiacetals formed from the reaction between acetaldehyde with methanol and isopropanol (m/z 75/103) and for the adducts formed between these anions and one (m/z 297/325) or two RDX (m/z 519/547) molecules.

The CID fragmentation patterns of the RDX adducts ions at m/z 325 and m/z 547 show the loss of one hemiacetal (-103) and the loss of one RDX molecule (-222) giving product ions at m/z 221 (RDX - H) and m/z 325 ($RDX + C_5H_{11}O_2^-$), respectively. This fragmentation mechanism is analogous to that for RDX adducted to the hemiacetal anion at m/z 75.

References

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