

H₃O⁺, NO⁺ and O₂⁺ as precursor ions in PTR-MS: isomeric VOC especially compounds and reactions with different chemical groups

A. Jordan¹, S. Jaksch¹, S. Jürschik^{1,2}, A. Edtbauer¹, B. Agarwal², G. Hanel¹, E. Hartungen¹, H. Seehauser¹, L. Märk¹, P. Sulzer¹ and T. D. Märk^{1,2}



IONICON ANALYTIK

¹ IONICON Analytik Gesellschaft m.b.H., Eduard-Bodem-Gasse 3, A-6020 Innsbruck, Austria

² Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens Universität, Technikerstr. 25, A-6020 Innsbruck, Austria

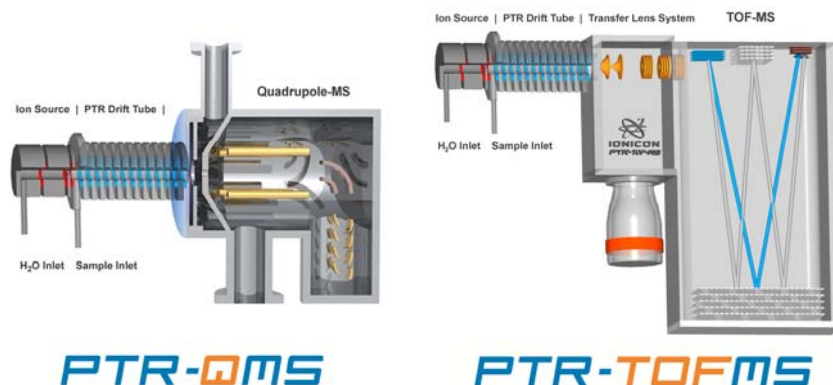
Abstract

Most Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) instruments employed so far use an ion source consisting of a hollow cathode discharge in water vapor which provides an intense source of protonated water (H₃O⁺). For a detailed description of the technique and established fields of application see [1] and the recent review [2]. However, the use of other ions, e.g. NO⁺ and O₂⁺, can be useful for the identification of VOCs, for separation of isomers and for the detection of VOCs with proton affinities below that of H₂O [3].

For certain chemical compound groups these different precursor ions show characteristic reaction paths and different product ions and especially charge transfer leads very often to different product ions for isomeric compounds.

In general the main advantage of O₂⁺ is to ionize compounds which are not measurable with protonated water. For example nearly all halogenated hydrocarbons are detectable with O₂⁺ whereas just the very large ones and the aromatic halogenated compounds are detectable with H₃O⁺.

By using NO⁺ as precursor ion in nearly all cases the product ions are different from the product ion by using protonated water. Very often also isomeric compounds show different product ions. For instance, isomers like aldehydes and ketones or acids and esters show in many cases different product ions in the reaction with NO⁺.



Experimental Setup

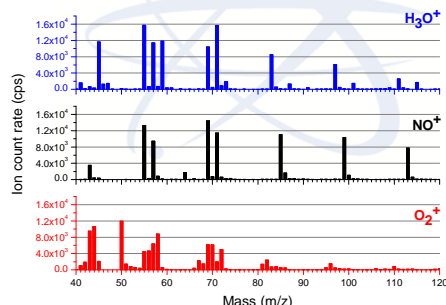
PTR+SRI-MS SWITCHABLE REAGENT IONS

Halocarbons

Halocarbons	Formula	H ₃ O ⁺ Reaction	NO ⁺ Reaction	O ₂ ⁺ Reaction
Methylchlorid	CH ₃ Cl			CH ₂ Cl ⁺
Vinylchlorid	C ₂ H ₃ Cl			C ₂ H ₂ Cl ⁺
Ethylchlorid	C ₂ H ₅ Cl			C ₂ H ₄ Cl ⁺
Methylenchlorid	CH ₂ Cl ₂			CHCl ₂ ⁺
Bromomethan	CH ₃ Br			CH ₂ Br ⁺
1,2-Dichloroethylen	C ₂ H ₄ Cl ₂	C ₂ H ₃ ClH ⁺ (100)	C ₂ H ₃ ClH ⁺ (100)	C ₂ H ₂ Cl ₂ ⁺
1,1-Dichloroethylen	C ₂ H ₃ Cl ₂			C ₂ H ₂ Cl ₂ ⁺
1,2-Dichloroethan	C ₂ H ₄ Cl ₂			C ₂ H ₃ Cl ₂ ⁺
1,3-Dichloroethan	C ₂ H ₄ Cl ₂			C ₂ H ₃ Cl ₂ ⁺
1,1,3-Dichloropropen	C ₃ H ₃ Cl ₃			C ₃ H ₂ Cl ₃ ⁺
c-1,3-Dichloropropen	C ₃ H ₃ Cl ₃			C ₃ H ₂ Cl ₃ ⁺
Chlorobenzene	C ₆ H ₅ Cl	C ₆ H ₄ ClH ⁺ (100)	C ₆ H ₄ ClH ⁺ (100)	C ₆ H ₄ Cl ⁺
1,2-dichloropropan	C ₃ H ₅ Cl ₂			C ₃ H ₄ Cl ₂ ⁺
Chloroform	CHCl ₃			CCl ₃ ⁺
Dichlorodifluoromethan	CF ₂ Cl ₂			CFCl ₂ ⁺
Trichloroethylen	C ₂ HCl ₃	C ₂ HCl ₂ H ⁺ (100)		CCl ₃ ⁺
1,1,1-trichloroethan	C ₂ HCl ₃			C ₂ HCl ₂ ⁺
1,1,2-trichloroethan	C ₂ HCl ₃			C ₂ HCl ₂ ⁺
1,1,2-trichlorofluoromethan	CFCl ₂			CFCl ₂ ⁺
1,2-dichlorobenzene	C ₆ H ₄ Cl ₂	C ₆ H ₃ Cl ₂ H ⁺ (100)	C ₆ H ₃ Cl ₂ H ⁺ (100)	C ₆ H ₂ Cl ₂ ⁺
1,3-dichlorobenzene	C ₆ H ₄ Cl ₂			C ₆ H ₃ Cl ₂ ⁺
1,4-dichlorobenzene	C ₆ H ₄ Cl ₂			C ₆ H ₃ Cl ₂ ⁺
Carbonotetrachlorid	CCl ₄			CCl ₃ ⁺
Tetrachloroethylen	C ₂ Cl ₄			C ₂ Cl ₃ ⁺
1,1,2,2-tetrachloroethan	C ₂ H ₂ Cl ₄			C ₂ HCl ₃ ⁺
1,2-dichlorotetrafluoräthan	C ₂ Cl ₂ F ₂			C ₂ ClF ₂ ⁺
1,2,4-trichlorobenzene	C ₆ H ₃ Cl ₃	C ₆ H ₂ Cl ₃ H ⁺ (100)	C ₆ H ₂ Cl ₃ H ⁺ (100)	C ₆ H ₂ Cl ₃ ⁺
1,1,2-trichlorodifluoräthan	C ₂ Cl ₂ F ₂			C ₂ ClF ₂ ⁺
Dibromomethan	CH ₂ Br ₂			C ₂ HBr ₂ ⁺
Hexachloro-1,3-butadien	C ₄ Cl ₆			C ₄ Cl ₅ ⁺

In "classical" PTR-MS water vapor originating from a reservoir filled with distilled water enters a hollow cathode ion source, where the H₃O⁺ is transformed into H₂O⁺ (primary ions). Due to the sophisticated design of the ion source, this process is highly efficient, i.e. the purity of the primary ions is greater than 99%, which means that no signal-diminishing mass filter (as is used by techniques similar to PTR-MS like e.g. SIFT) is needed between the ion source and the adjacent drift tube. The actual ionization of the trace compounds present in the sample air takes place in the drift tube via proton transfer from H₃O⁺ to all molecules that possess a higher proton affinity than water. As all major air components (N₂, O₂, CO₂, Ar, etc.) have lower proton affinities than water, the air itself acts as a buffer gas and no additional gas supply is needed for the operation of a PTR-MS instrument. Depending on the kind of instrument the protonated molecules are subsequently introduced into either a quadrupole mass filter or a time-of-flight (TOF) mass analyzer. Above, two schematic drawings of quadrupole and TOF based PTR-MS instruments are presented.

With the Switchable Reagent Ions (SRI) feature additionally O₂⁺ and NO⁺ can be used as primary ions. NO⁺ is generated from normal air whereas for the operation with O₂⁺ an oxygen supply is necessary. However, the principal instrumental setup stays the same, i.e. no mass filter is needed for the selection of the primary ions.



The diagrams on the left show a comparison of mass spectra obtained from 8 aldehydes using H₃O⁺, NO⁺ and O₂⁺. It can be easily seen that NO⁺ leads to the simplest spectrum mainly giving dehydrogenated cations (M-H)⁺. O₂⁺ on the other hand reacts via exothermic charge transfer resulting in strong fragmentation, whereas proton transfer from H₃O⁺ produces mostly protonated parent molecules (MH⁺).

Organosulphurs

Organosulphur compounds	Formula	H ₃ O ⁺ Reaction	NO ⁺ Reaction	O ₂ ⁺ Reaction
Carbon disulfide	CS ₂	CS ₂ H ⁺ (100) + H ₂ O		
Methanethiol	CH ₃ SH	C ₂ H ₅ SH ⁺ (100) + H ₂ O	C ₂ H ₅ SH ⁺ (80) + H ₂ O	C ₂ H ₅ S ⁺ (100) + H ₂ O
Dimethylsulfid	C ₂ H ₆ S	C ₂ H ₅ SH ⁺ (100) + H ₂ O	C ₂ H ₅ S ⁺ (100) + H ₂ O	C ₂ H ₅ SH ⁺ (100) + H ₂ O
Ethandiol	C ₂ H ₆ OS	C ₂ H ₅ SH ⁺ (100) + H ₂ O	C ₂ H ₅ S ⁺ (100) + H ₂ O	C ₂ H ₅ SH ⁺ (100) + H ₂ O
Dimethylsulfid	C ₂ H ₆ S	C ₂ H ₅ SH ⁺ (100) + H ₂ O	C ₂ H ₅ S ⁺ (100) + H ₂ O	C ₂ H ₅ SH ⁺ (100) + H ₂ O
Thioacetid	CH ₃ COSH	CH ₃ COSH ⁺ (80) + H ₂ O	CH ₃ CO ⁺ (100) + H ₂ O	CH ₃ COSH ⁺ (80) + H ₂ O
Dialylsulfid	C ₄ H ₈ S	C ₄ H ₇ SH ⁺ (100) + H ₂ O	C ₄ H ₇ S ⁺ (100) + H ₂ O	C ₄ H ₇ SH ⁺ (100) + H ₂ O

Acids

Carboxylic acids	Formula	H ₃ O ⁺ Reaction	NO ⁺ Reaction	O ₂ ⁺ Reaction
Formic acid	HOOC	HOOC(H ₂ O) ⁺ (95) + H ₂ O		HOOC(H ₂ O) ⁺ (95)
Acetic acid	CH ₃ COOH	CH ₃ COOH(H ₂ O) ⁺ (80) + H ₂ O	CH ₃ COOH(H ₂ O) ⁺ (80) + H ₂ O	CH ₃ COOH(H ₂ O) ⁺ (80)
Propionic acid	C ₂ H ₅ COOH	C ₂ H ₅ COOH(H ₂ O) ⁺ (70) + H ₂ O	C ₂ H ₅ COOH(H ₂ O) ⁺ (70) + H ₂ O	C ₂ H ₅ COOH(H ₂ O) ⁺ (70)
n-butiric acid	C ₃ H ₇ COOH	C ₃ H ₇ COOH(H ₂ O) ⁺ (70) + H ₂ O	C ₃ H ₇ COOH(H ₂ O) ⁺ (70) + H ₂ O	C ₃ H ₇ COOH(H ₂ O) ⁺ (70)
isobutiric acid	C ₄ H ₉ COOH	C ₄ H ₉ COOH(H ₂ O) ⁺ (70) + H ₂ O	C ₄ H ₉ COOH(H ₂ O) ⁺ (70) + H ₂ O	C ₄ H ₉ COOH(H ₂ O) ⁺ (70)
Valeric acid	C ₄ H ₉ COOH	C ₄ H ₉ COOH(H ₂ O) ⁺ (70) + H ₂ O	C ₄ H ₉ COOH(H ₂ O) ⁺ (70) + H ₂ O	C ₄ H ₉ COOH(H ₂ O) ⁺ (70)
Azylid acid	C ₂ H ₃ COOH	C ₂ H ₃ COOH(H ₂ O) ⁺ (100) + H ₂ O	C ₂ H ₃ COOH(H ₂ O) ⁺ (100) + H ₂ O	C ₂ H ₃ COOH(H ₂ O) ⁺ (100)
Lactic acid	C ₃ H ₅ COOH	C ₃ H ₅ COOH(H ₂ O) ⁺ (100) + H ₂ O	C ₃ H ₅ COOH(H ₂ O) ⁺ (100) + H ₂ O	C ₃ H ₅ COOH(H ₂ O) ⁺ (100)

Results

Esters

Ester compounds	Formula	H ₃ O ⁺ Reaction	NO ⁺ Reaction	O ₂ ⁺ Reaction
Methyl formate	HCOC(=O)CH ₃	HCOC(=O)CH ₃ (H ₂ O) ⁺ (80) + H ₂ O	NOHCOC(=O)CH ₃ (H ₂ O) ⁺ (100) + H ₂ O	HCOC(=O)CH ₃ (H ₂ O) ⁺ (80) + H ₂ O
Ethyl formate	HCOC(=O)C ₂ H ₅	HCOC(=O)C ₂ H ₅ (H ₂ O) ⁺ (90) + H ₂ O	NOHCOC(=O)C ₂ H ₅ (H ₂ O) ⁺ (100) + H ₂ O	HCOC(=O)C ₂ H ₅ (H ₂ O) ⁺ (90) + H ₂ O
Methyl acetate	CH ₃ COOC(=O)CH ₃	CH ₃ COOC(=O)CH ₃ (H ₂ O) ⁺ (100) + H ₂ O	NOHCOC(=O)CH ₃ (H ₂ O) ⁺ (100) + H ₂ O	CH ₃ COOC(=O)CH ₃ (H ₂ O) ⁺ (100) + H ₂ O
Ethyl acetate	CH ₃ COOC(=O)C ₂ H ₅	CH ₃ COOC(=O)C ₂ H ₅ (H ₂ O) ⁺ (100) + H ₂ O	NOHCOC(=O)C ₂ H ₅ (H ₂ O) ⁺ (100) + H ₂ O	CH ₃ COOC(=O)C ₂ H ₅ (H ₂ O) ⁺ (100) + H ₂ O
Methyl propionate	C ₂ H ₅ COOC(=O)CH ₃	C ₂ H ₅ COOC(=O)CH ₃ (H ₂ O) ⁺ (70) + H ₂ O	NOHCOC(=O)CH ₃ (H ₂ O) ⁺ (100) + H ₂ O	C ₂ H ₅ COOC(=O)CH ₃ (H ₂ O) ⁺ (70) + H ₂ O
Ethyl propionate	C ₂ H ₅ COOC(=O)C ₂ H ₅	C ₂ H ₅ COOC(=O)C ₂ H ₅ (H ₂ O) ⁺ (70) + H ₂ O	NOHCOC(=O)C ₂ H ₅ (H ₂ O) ⁺ (100) + H ₂ O	C ₂ H ₅ COOC(=O)C ₂ H ₅ (H ₂ O) ⁺ (70) + H ₂ O
Methyl butyrate	C ₃ H ₇ COOC(=O)CH ₃	C ₃ H ₇ COOC(=O)CH ₃ (H ₂ O) ⁺ (70) + H ₂ O	NOHCOC(=O)CH ₃ (H ₂ O) ⁺ (100) + H ₂ O	C ₃ H ₇ COOC(=O)CH ₃ (H ₂ O) ⁺ (70) + H ₂ O

Aromatics

Aromatic compounds	Formula	H ₃ O ⁺ Reaction	NO ⁺ Reaction	O ₂ ⁺ Reaction
Benzene	C ₆ H ₆	C ₆ H ₅ H ⁺ (100) + H ₂ O	C ₆ H ₅ ⁺ (100) + H ₂ O	C ₆ H ₅ H ⁺ (100) + H ₂ O
Toluene	C ₇ H ₈	C ₇ H ₇ H ⁺ (100) + H ₂ O	C ₇ H ₇ ⁺ (100) + H ₂ O	C ₇ H ₇ H ⁺ (100) + H ₂ O
Styrene	C ₈ H ₈	C ₈ H ₇ H ⁺ (100) + H ₂ O	C ₈ H ₇ ⁺ (100) + H ₂ O	C ₈ H ₇ H ⁺ (100) + H ₂ O
o-xylene	C ₈ H ₁₀	C ₈ H ₉ H ⁺ (100) + H ₂ O	C ₈ H ₉ ⁺ (100) + H ₂ O	C ₈ H ₉ H ⁺ (100) + H ₂ O
m-xylene	C ₈ H ₁₀	C ₈ H ₉ H ⁺ (100) + H ₂ O	C ₈ H ₉ ⁺ (100) + H ₂ O	C ₈ H ₉ H ⁺ (100) + H ₂ O
p-xylene	C ₈ H ₁₀	C ₈ H ₉ H ⁺ (100) + H ₂ O	C ₈ H ₉ ⁺ (100) + H ₂ O	C ₈ H ₉ H ⁺ (100) + H ₂ O
Ethyl-benzene	C ₈ H ₁₀	C ₈ H ₉ H ⁺ (100) + H ₂ O	C ₈ H ₉ ⁺ (100) + H ₂ O	C ₈ H ₉ H ⁺ (100) + H ₂ O
Trimethylbenzene	C ₉ H ₁₂	C ₉ H ₁₁ H ⁺ (100) + H ₂ O	C ₉ H ₁₁ ⁺ (100) + H ₂ O	C ₉ H ₁₁ H ⁺ (100) + H ₂ O
Chlorobenzene	C ₆ H ₅ Cl	C ₆ H ₄ ClH ⁺ (100) + H ₂ O	C ₆ H ₄ Cl ⁺ (100) + H ₂ O	C ₆ H ₄ ClH ⁺ (100) + H ₂ O
1,2-Dichlorobenzene	C ₆ H ₄ Cl ₂	C ₆ H ₃ Cl ₂ H ⁺ (100) + H ₂ O	C ₆ H ₃ Cl ₂ ⁺ (100) + H ₂ O	C ₆ H ₃ Cl ₂ H ⁺ (100) + H ₂ O
1,3-Dichlorobenzene	C ₆ H ₄ Cl ₂	C ₆ H ₃ Cl ₂ H ⁺ (100) + H ₂ O	C ₆ H ₃ Cl ₂ ⁺ (100) + H ₂ O	C ₆ H ₃ Cl ₂ H ⁺ (100) + H ₂ O
Trichlorobenzene	C ₆ H ₃ Cl ₃	C ₆ H ₂ Cl ₃ H ⁺ (100) + H ₂ O	C ₆ H ₂ Cl ₃ ⁺ (100) + H ₂ O	C ₆ H ₂ Cl ₃ H ⁺ (100) + H ₂ O

Aldehydes

Aldehydes	Formula	H ₃ O ⁺ Reaction	NO ⁺ Reaction
Formaldehyd	HCHO	CH ₂ O ⁺ (100) + H ₂ O	
Acetaldehyd	CH ₃ CHO	C ₂ H ₃ O ⁺ (100) + H ₂ O	C ₂ H ₂ O ⁺ + HNO
Acrolein	C ₂ H ₃ CHO	C ₂ H ₂ O ⁺ (100) + H ₂ O	C ₂ H ₂ O ⁺ + HNO
1-propanal	C ₂ H ₅ CHO	C ₂ H ₄ O ⁺ (85) + H ₂ O	C ₂ H ₃ O ⁺ + HNO
Crotonaldehyd	C ₄ H ₇ CHO	C ₄ H ₆ O ⁺ (100) + H ₂ O	C ₄ H ₅ O ⁺ + HNO
1-butanal	C ₃ H ₇ CHO	C ₃ H ₆ O ⁺ (100) + H ₂ O	C ₃ H ₅ O ⁺ + HNO
Valeraldehyd	C ₄ H ₉ CHO	C ₄ H ₈ O ⁺ (100) + H ₂ O	C ₄ H ₇ O ⁺ + HNO
Hexanal	C ₅ H ₁₁ CHO	C ₅ H ₁₀ O ⁺ (100) + H ₂ O	C ₅ H ₉ O ⁺ + HNO
Heptanal	C ₆ H ₁₃ CHO	C ₆ H ₁₂ O<	