



PTR-MS fragmentation patterns of gasoline hydrocarbons



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ABSTRACT

Product ion yields for a suite of hydrocarbons associated with motor vehicle exhaust including alkenes, alkanes, cycloalkanes, and aromatic compounds are reported for a PTR-MS instrument operated at an E/N ratio of 80 and 120 Td. At 120 Td many of the compounds tested underwent dissociative proton transfer reactions complicating the interpretation of the vehicle exhaust mass spectrum. However at 80 Td most aromatic and alkene compounds tested yielded $M+H$ product ions at near 100% yield and alkyl substituted cyclohexanes and C_9 – C_{12} branched alkanes yielded $M-H$ ions as the major product ion. The PTR-MS response factors to dimethyl and trimethyl cyclohexane compounds were about a third of that expected if they reacted at the collisional rate limit with H_3O^+ . Analysis of gasoline at 80 Td showed that the major peaks in the mass spectrum could be reasonably accounted for from known hydrocarbon abundance and their product ion yields, including the alkyl substituted cyclohexane compounds which yielded $M-H$ ions at m/z 97, 111, and 125. Operation at lower E/N ratios would enable the PTR-MS to measure alkyl substituted cyclohexanes and larger alkane compounds in urban air at their $M-H$ product ion.

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1. Introduction

Vehicle emissions are major sources of volatile organic compounds (VOC) in urban areas. Measuring the abundance of organic compounds emitted from vehicles is important for assessing the impact of vehicle emissions on human health [11] and on the generation of secondary photochemical pollutants such as ozone and secondary organic aerosol [26]. Measurement of organic trace gases in the atmosphere is typically done using gas chromatography, allowing for analysis of selected C_1 – C_{12} compounds by either grab sample collection (i.e. [38,1]) or in-situ sampling and analysis (i.e. [39,25]). Another measurement approach using the proton transfer reaction mass spectrometer (PTR-MS) instrument has seen increased use by the research community in urban field studies [18,28,12,17]. The PTR-MS instrument provides a less detailed account of the organic chemical composition of urban air but it does have some advantages. One advantage is that the PTR-MS measures important oxygenated compounds such as formaldehyde and acetaldehyde that are difficult to sample and measure by gas chromatography. These aldehydes are important constituents of vehicle exhaust and are also created in photochemical oxidation reactions of VOCs. The in-situ, high time resolution measurements of the PTR-MS can also be advantageous when there is a need to follow rapid changes in concentrations in ambient air such as in

near-roadway monitoring and in measuring statistical relationships between VOCs and other pollutants such as carbon monoxide (CO) and nitrogen oxides (NOx) for source apportionment studies.

The mass spectrum of the PTR-MS is ideally interpreted as an $M+H$ mass spectrum (molecular weight + 1), but many proton transfer reactions with organic compounds found in urban air are known to be dissociative, making the interpretation of the mass spectrum subject to uncertainty. The fragmentation of alcohols, aldehydes, aromatics, alkanes, alkenes, ketones, esters, and monoterpenes has been documented in the literature [4,35,15,19,3,8]. The chemical composition of urban air is principally a result of vehicle emissions which contribute alkanes, cycloalkanes, alkenes, aromatics, and aldehydes as major constituents ([29,30,27,23]). Given the large number of compounds present, the fidelity and information content of the PTR-MS mass spectrum of urban air is not well understood and limits its usefulness as a VOC monitor. Compounds reported from PTR-MS urban air measurements tend to focus on monoaromatic compounds and light oxygenated compounds [18,12,28,14] as these compounds are thought to have little interference caused by fragmentation of other organic compounds. Intercomparisons between GC-MS and PTR-MS measurements for urban air are relatively few and sometimes illustrate inherent problems with PTR-MS operating conditions and compound fragmentation [20,17].

A better understanding of the PTR-MS fragmentation patterns of vehicle exhaust would allow for a more complete understanding of the information available from PTR-MS measurements of

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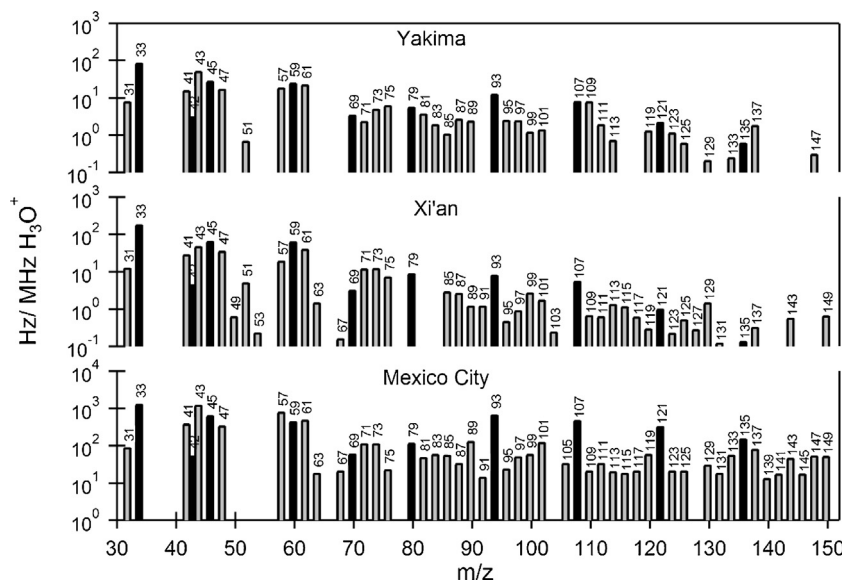


Fig. 1. PTR-MS mass spectrum from m/z 30 to m/z 150 of ambient air measurement obtained from three cities: Mexico City, Mexico in March 2006 (bottom), Xi'an China in August 2011 (middle) and Yakima, WA in January 2013 (top). All data collected at 120 Td. Black bars indicate ions that have been typically reported as having a reasonably well defined attribution to a particular compound(s): m/z 33 = methanol, 42 = acetonitrile, 45 = acetaldehyde, 59 = acetone & propanal, 69 = isoprene, 79 = benzene, 93 = toluene, 107 = sum C_2 -alkylbenzene isomers and benzaldehyde, 121 = sum of C_3 -alkylbenzene isomers, 135 = sum of C_4 -alkylbenzene isomers.

urban air and PTR-MS measurement fidelity. Examples of urban air PTR-MS mass spectrum are displayed in Fig. 1, showing data from Mexico City, Mexico [36], Xi'an, China, and a much smaller city, Yakima, WA. The data were collected using the same PTR-MS instrument operated under the same drift tube operation conditions of 120 Td. Both the Mexico and Yakima data were collected in the morning during a period of higher mixing ratios caused by lower mixed layer heights and significant emissions from motor vehicles during the morning rush hour. The wintertime conditions of Yakima preclude much photochemical activity so the mass spectrum reflects primary emissions. As expected, given its much larger emissions, Mexico City air is more polluted than Yakima by a factor of 10–100 and the signal is significantly dominated by the monoaromatic compounds at m/z 93, 107, 121, 135. There is significant ion signal at many other masses, yet this data is not used because of uncertainties in the attribution to specific compounds. Of interest in this paper is the significant ion signal at m/z 97, 99, 111, 113, 119, 123, 125 that are likely from compounds emitted in vehicle exhaust. Also of note is the winter time abundance of m/z 69 and m/z 137 in Yakima. These masses are commonly attributed to the biogenic compounds, isoprene and monoterpenes respectively, but these compounds would not be emitted in this region in winter. A more likely attribution is from organic compounds associated with anthropogenic emissions, such as vehicles or residential wood burning. Resolving fragmentation patterns or reducing fragmentation for compounds commonly emitted from vehicle exhaust would facilitate the interpretation of PTR-MS data and broaden its usefulness as an urban air quality monitoring tool. In this paper we show fragmentation patterns of some of the most abundant compounds found in gasoline engine exhaust for two PTR-MS operating conditions: 80 and 120 Td. We show that operation of the PTR-MS drift tube at 80 Td yields an $M+H$ and $M-H$ mass spectrum for most compounds, whereas at the typical operating condition of 120 Td many compounds fragment, reducing the utility of the PTR-MS as an urban air quality monitoring instrument.

2. Experimental

VOC measurements by the PTR-MS are based on a soft ionization of the organic compounds with the hydronium ion H_3O^+ . The

method has been well described in literature [22,6]. Organic compounds (R) with proton affinities greater than that of water undergo fast proton transfer reactions with H_3O^+



where R is the organic compound and RH^+ is the measured product ion. The reaction occurs in an ion drift tube that enhances the kinetic energy of the ions so that collisions with the bath gas (air) cause desolvation of hydrated ions. In Fig. 2, the proton affinities of the major organics reported from vehicle exhaust measurements are illustrated. Water cluster formation is a strong function of the drift tube pressure and electric field and these are typically adjusted to limit

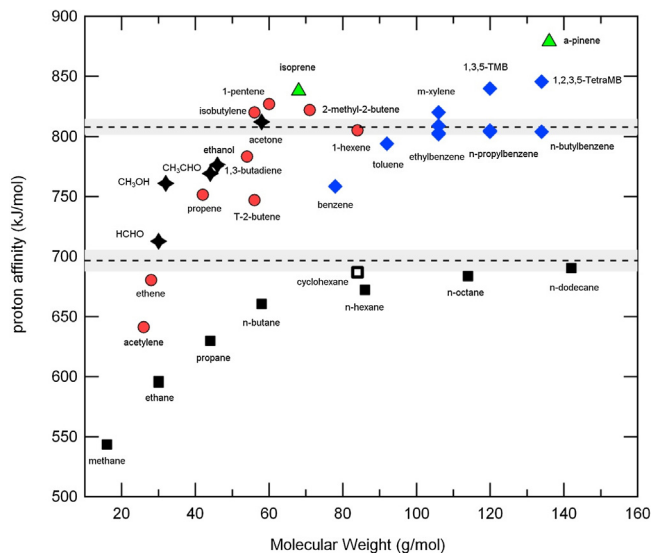


Fig. 2. Proton affinities of some compounds found in urban air including alkenes (red circles), aromatics (blue diamond), alkanes (black squares), oxygenated compounds (stars), cycloalkanes (white squares) identified in vehicle exhaust, and biogenic compounds (green triangles). The proton affinity of water (691 kJ/mol) and the water dimer (808 kJ/mol) is represented by the dashed line with shading representing reported uncertainty. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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