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Hydrocarbon analysis using desorption atmospheric pressure chemical ionization

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ABSTRACT

Characterization of the various petroleum constituents (hydronaphthalenes, thiophenes, alkyl substituted benzenes, pyridines, fluorenes, and polycyclic aromatic hydrocarbons) was achieved under ambient conditions without sample preparation by desorption atmospheric pressure chemical ionization (DAPCI). Conditions were chosen for the DAPCI experiments to control whether ionization was by proton or electron transfer. The protonated molecule $[M+H]^+$ and the hydride abstracted $[MH]^+$ form were observed when using an inert gas, typically nitrogen, to direct a lightly ionized plasma generated by corona discharge onto the sample surface in air. The abundant water cluster ions generated in this experiment react with condensed-phase functionalized hydrocarbon model compounds and their mixtures at or near the sample surface. On the other hand, when naphthalene was doped into the DAPCI gas stream, its radical cation served as a charge exchange reagent, yielding molecular radical cations $(M^{+\bullet})$ of the hydrocarbons. This mode of sample ionization provided mass spectra with better signal/noise ratios and without unwanted side-products. It also extended the applicability of DAPCI to petroleum constituents which could not be analyzed through proton transfer (e.g., higher molecular PAHs such as chrysene). The thermochemistry governing the individual ionization processes is discussed and a desorption/ionization mechanism is inferred.

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1. Introduction

Mass spectrometry (MS) is the gold standard method for trace detection of a wide range of analytes due to its high sensitivity and specificity and, through tandem mass spectrometry (MS/MS), [1,2] applicability to complex mixture analysis. As the utilization of MS has increased, so has interest in its applicability to in situ analysis of samples in the open environment. In situ experiments require suitable portable instrumentation capable of MS/MS [3–8] as well as ionization methods that operate under ambient conditions without requiring prior sample preparation. Such methods will allow non-specialists to use MS in the field and to obtain immediate results. The advent of ambient ionization techniques has enabled the mass spectrometric analysis of chemical compounds from unmodified surfaces in their native environments [9–15]. The most commonly used ambient ionization methods are the spray-based method of desorption electrospray ionization (DESI) [11,16] and the plasma-based method known as direct analysis in real time (DART) [17]. The analytical capabilities of the various ambient ionization methods have been demonstrated through applications in biomedicine such as in tissue imaging and biofluid analysis [18–20], in chemical imaging and forensics [21], in environmental monitoring and food safety [22], and in pharmaceutical science as well as in transportation security [23].

Desorption atmospheric pressure chemical ionization (DAPCI) [24] is another example of a plasma-based ambient ionization technique but one which is relatively under-utilized compared to DART and low temperature plasma (LTP) ionization [25]. DAPCI is derived from atmospheric pressure chemical ionization (APCI) [26] although DAPCI produces ions from solids in the open air instead of from solutions or vapors. In DAPCI, a corona discharge is generated by applying a high DC voltage to a sharp needle and the reagent ions produced are directed pneumatically toward a surface using a high velocity carrier gas (e.g., nitrogen). Analyte is desorbed and ionized directly from the surface, presumably by a two-step mechanism involving thermal desorption followed by gas-phase ionization [24]. Earlier experiments demonstrated DAPCI to be more effective at ionizing compounds of moderate to low polarity and hence significant vapor pressure [4]. Performing DAPCI experiments in ambient air generates protonated water cluster ions which facilitate analyte ionization [24]. Using water clusters as the primary ion species, DAPCI ion sources have been used in agriculture and food chemistry to characterize various natural products [27]

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and to detect explosives, herbicides and simulants on a variety of surfaces, including skin [24,25]. Using methanol/water vapor as the carrier gas, the stimulant dimethyl methyl phosphonate (DMMP) displayed low detection limits using DAPCI compared to DESI [24]. Furthermore, peroxide explosives have been identified at lower detection limits using alternative reagent ions, specifically ammonium reagent ions instead of methanol/water vapors [28]. Aside from moderating the degree of proton transfer by selecting appropriate solvent vapors for DAPCI, charge exchange reagents (e.g., benzene and fluorobenzene) can also be doped into the gas stream to initiate electron transfer reactions [29,30]. Analogous conditions have been found to be useful in DART for the analysis of analyte(s) such as hydrocarbons, which have low proton affinities and cannot be effectively protonated by protonated water clusters [30]. Charge exchange is also the basis of a related ambient ionization method, termed desorption charge exchange ionization (DICE)[31] which differs from DAPCI in that it uses a stream of charged droplets but is related in that it uses an easily ionized solvent like toluene.

In this study, we investigate the applicability of DAPCI to analyze different petroleum constituents using the two different modes of ionization (i.e., proton versus electron transfer) at ambient surfaces. Naphthalene vapor was doped into the DAPCI carrier gas as the charge exchange reagent for the electron transfer reactions. The two ionization modes were used to sample petroleum hydrocarbon constituents such as hydronaphthalenes, thiophenes, substituted alkyl benzenes, pyridines, fluorenes, polycyclic hydrocarbons, and *n*-alkanes under ambient conditions. Radical cations and protonated molecules were generated during electron and proton transfer ionization modes, respectively, with the electron transfer process often producing a simpler mass spectrum. The electron transfer ionization mode also extended the range of DAPCI applications to higher molecular compounds such as polycyclic aromatic hydrocarbons that could not be ionized via proton attachment. In addition to protonation, other reactions such as hydride abstraction (sometimes followed by hydration of the resulting $[M-H]^+$ ions) as well as oxidation of certain hydrocarbons were also observed and complicated DAPCI spectra in the absence of a charge exchange reagent like naphthalene.

2. Experimental

2.1. Chemicals and reagents

1,4-Dihydronaphthalene, 1,2-dihydronaphthalene, 1,2,3,4-tetrahydronaphthalene, dibenzothiophene, 2,2'-bithiophene, 1,8-dinapthylenethiophene, 1,2,3,4-tetramethylbenzene, pentamethylbenzene, hexamethylbenzene, 2, 6-diphenylpyridine, 3-butylpyridine, 3-phenylpyridine, 9-ethylfluorene, 1-methylfluorene, 9-phenylfluorene, (11H)-benzo-beta-fluorene, hexadecane, docosane, triacontane, icosane, octadecane, and naphthalene-d8 were purchased from Sigma–Aldrich Inc (Milwaukee, WI, USA), whereas chrysene, benzo(ghi)perylene, pyrene, fluorene, phenanthrene, fluoranthene and acenaphthylene were obtained from Supelco Analytical (Bellefonte, PA USA). Naphthalene was obtained from Fisher Scientific (Fair Lawn, NJ, USA) and chloroform (HPLC grade) from Mallinckrodt Baker Inc. (Phillipsburg, NJ). Gas/diesel standard mixtures were obtained from Cerilliant Corporation (Round Rock, Texas, USA). Compounds in the liquid phase were used in their pure form without any dilution or sample pretreatment whereas 3–10 mg of solid samples were dissolved into 10–100 μL of chloroform or methanol and 1–3 μL of each sample was deposited on a filter paper surface for analysis by DAPCI-MS.

2.2. Desorption atmospheric pressure chemical ionization mass spectrometry

The configuration of the DAPCI system used here was identical to that described earlier [24,25]; it consists of a stainless steel needle with an elongated tapered tip, connected to a high voltage power supply (Fig. 1). The elongated tip projects from a Teflon capillary tube carrying a high velocity flow of gas. The carrier gas is directed toward a substrate/surface to desorb and ionize analytes which may be present. The carrier gas can be an inert gas such as N_2 or He. The voltage applied to the electrode was typically between about 3 and 3.5 kV so as to produce a corona discharge in close proximity to the tip of electrode. In some experiments, naphthalene vapor was introduced by placing cotton soaked in a 10 ppm solution of naphthalene in chloroform in the DAPCI source to cause charge transfer reactions. The ion source is coupled to a suitable mass spectrometer simply by placingd it near the atmospheric inlet. The system provides high sensitivity, applicability to nonvolatile and thermally unstable analytes and with high chemical specificity through the MS/MS experiment.

Experiments were performed using a Thermo LTQ linear ion trap mass spectrometer (Thermo Scientific San Jose, CA) tuned for optimum detection of the precursor ion of interest in the positive mode. The DAPCI ion source was placed 2–3 mm in front of the MS inlet capillary and set at 45o to the sample surface as shown in Fig. 1. The potential on the needle was set to 3.5 kV to generate a corona discharge that is carried by the nitrogen carrier gas at a flow rate of 1 L/min. Primary ions are generated in the carrier gas by traces of impurities especially water. The resulting water cluster ions impact the sample surface for desorption/ionization so that ions of the analytes are created under ambient conditions. The analyte ions are then transferred into the LTQ mass analyzer for mass analysis via the ion guide system of the instrument. The LTQ mass spectrometer was set to operate in the positive ion mode and the capillary voltage set to 15 V, temperature set to 150 °C, while the tube lens voltage was set at 65 V.

All mass spectra were recorded as peak profiles with averaging time of 1 min and were background subtracted unless otherwise stated. MS/MS was performed on the molecular ion signals of interest, isolated using mass windows of 1–2 *m/z* units and using 15–45 eV collision energy in all experiments.

3. Results and discussion

Fig. 2a is a typical background mass spectrum recorded using the normal DAPCI experimental conditions in which only a corona discharge and nitrogen carrier gas are used. This mass spectrum shows predominantly the presence of protonated water clusters $H[H_2O]_2^+$ and $H[H_2O]_3^+$ at *m/z* 37 and 55, respectively. Highly volatile solvents in the laboratory environment produce background peaks at *m/z* 33, 42 and 60 corresponding to protonated methanol, acetonitrile, and acetone, respectively. On the other hand, a completely different background spectrum with better signal/noise ratios resulted (Fig. 2b) when the headspace vapor of naphthalene (ionization energy 8.1 eV, proton affinity 802.9 kJ mol^{-1}) was doped into the DAPCI gas stream. The spectrum typically showed naphthalene radical cation at *m/z* 128 along with related peaks at *m/z* 130, 144 and 157. By using naphthalene-d8 as the DAPCI charge exchange reagent, peaks at *m/z* 130 and 144, in the background were confirmed to be related to naphthalene. They appear to be due to (i) oxidation, leading to the addition of atomic oxygen to naphthalene at *m/z* 144 and (ii) reduction of naphthalene to give the ion of *m/z* 130. The origin of the background peak at *m/z* 157 marked by the asterisk is not known.