



Identification of primary amines in Titan tholins using microchip nonaqueous capillary electrophoresis



M.L. Cable^a, S.M. Hörst^b, C. He^c, A.M. Stockton^a, M.F. Mora^a, M.A. Tolbert^{b,d},
M.A. Smith^c, P.A. Willis^{a,*}

^a Instrument Electronics and Sensors Section, NASA Jet Propulsion Laboratory, Pasadena, CA 91109, United States

^b Cooperative Institute for Research in Environmental Sciences, University of Colorado–Boulder, Boulder, CO 80309, United States

^c Department of Chemistry, University of Houston, Houston, TX 77004, United States

^d Department of Chemistry and Biochemistry, University of Colorado Boulder, Boulder, CO 80309, United States

ARTICLE INFO

Article history:

Received 27 January 2014

Received in revised form 20 May 2014

Accepted 20 June 2014

Available online 14 July 2014

Editor: C. Sotin

Keywords:

Titan
microfluidics
ethanol
ethylamine
lab-on-a-chip

ABSTRACT

Titan, the moon of Saturn with a thick atmosphere and an active hydrocarbon-based weather cycle, is considered the best target in the solar system for the study of organic chemistry on a planetary scale. Microfluidic devices that employ liquid phase techniques such as capillary electrophoresis with ultrasensitive laser-induced fluorescence detection offer a unique solution for in situ analysis of complex organics on Titan. We previously reported a protocol for nonaqueous microfluidic analysis of primary aliphatic amines in ethanol, and demonstrated separations of short- and long-chain amines down to -20°C . We have optimized this protocol further, and used it to analyze Titan aerosol analogues (tholins) generated in two separate laboratories under a variety of different conditions. Ethylamine was a major product in all samples, though significant differences in amine content were observed, in particular for long-chain amines (C12–C27). This work validates microfluidic chemical analysis of complex organics with relevance to Titan, and represents a significant first step in understanding tholin composition via targeted functional group analysis.

© 2014 Published by Elsevier B.V.

1. Introduction

Titan has intrigued astronomers since its discovery, and with the recent insights and images from the Cassini–Huygens mission (Brown et al., 2009), this moon of Saturn has captivated both the scientific community and the general public. The presence of equatorial dunes and polar lakes is undeniably interesting, but what is more fascinating from a chemistry standpoint is what these dunes are composed of, and what molecules may be dissolved in the hydrocarbon lakes. Titan is host to an impressively complex chemical inventory, and by understanding the types and distribution of these organics, we may begin to understand prebiotic chemistry on a planetary scale.

Titan's thick (1.5 bar) atmosphere, composed of $\sim 2\%$ CH_4 and 98% N_2 (Cui et al., 2009; Flasar et al., 2005), is exposed to energetic inputs from solar radiation, cosmic radiation and energetic particles from Saturn's magnetosphere (Lavvas et al., 2011). The resulting activation of nitrogen and methane leads to a plethora of chemical reactions, generating complex organic aerosols that form haze layers and continue to grow through various processes as

they fall to the surface (Lavvas et al., 2013, 2008). This veneer of organic material coating the surface is most likely composed of both large and small molecules containing carbon, hydrogen and nitrogen, though the degree of saturation, extent of nitrogen incorporation and types of exposed functional groups present are unknown. Further, putative cryovolcanism (Lopes et al., 2013) and the occasional meteoritic impact (Artemieva and Lunine, 2003) could generate liquid melt pools and induce active chemistry on the surface (Neish et al., 2008; Poch et al., 2012).

To better understand Titan aerosol composition and reactivity, simulants of these organics have been generated in the laboratory. Termed 'tholins', these simulated Titan aerosols are highly varied in their production methods, which is reflected in their chemical composition (Table 1). Due to this variability in properties, there is some discussion in the literature as to which tholins are the most 'Titan-like', i.e., the closest physically and chemically to the aerosols on Titan (Cable et al., 2012; Dalba et al., 2012). Due to the complexity of these samples, most analytical techniques can only provide information on bulk properties (C/N ratio, refractive index) or the presence of particular chemical bonds (C–H, C \equiv N, etc.). Detailed structural information is limited to small molecular species where NMR and MS data can be easily deconvoluted. Unequivocal

* Corresponding author.

Table 1

Compounds generated by different tholin production methods starting with N₂ and CH₄, as reported in over 70 publications from 1975 to present. Percentage values and gray shading refer to the fraction of publications that report each compound class for a given production method. Reproduced in part from Cable et al. (2012) (see references therein) and updated with the following recent work: Carrasco et al. (2012), Derenne et al. (2012), Gautier et al. (2011, 2012a, 2012b), He et al. (2012a, 2012b), Hörst et al. (2012), Mahjoub et al. (2012), Peng et al. (2013), Somogyi et al. (2012), Thejaswini et al. (2011), Trainer et al. (2012).

Tholin Production Method		Compound									
		Saturated hydrocarbons (methane, ethane, etc.)	Aromatic hydrocarbons (benzene, naphthalene, etc.)	Unsaturated hydrocarbons (acetylene, alkynes, etc.)	Ammonia (NH ₃)	Amines (methylamine, ethylamine, etc.)	Imines (methanimine, ethanimine, etc.)	Nitriles (HCN, butanenitrile, etc.)	Heterocyclic compounds (benzimidazole, etc.)		
Cold plasma discharge		78%	46%	65%	11%	30%	16%	78%	27%		
Hot plasma discharge	Spark/arc discharge	43%	36%	64%	0%	14%	21%	71%	29		
	Laser-induced plasma	60%	40%	80%	0%	0%	0%	80%	0%		
UV irradiation	Short ($\lambda < 80$ nm)	100%	60%	80%	20%	20%	0%	60%	0%		
	Long ($\lambda > 100$ nm)	40%	40%	100%	0%	20%	0%	20%	0%		
Gamma rays, soft X-rays		67%	67%	100%	0%	0%	0%	100%	33%		
Electron beam bombardment		100%	0%	100%	0%	0%	0%	100%	0%		
Proton beam bombardment		67%	0%	100%	0%	33%	0%	100%	0%		

identification of specific functional groups in tholins would provide greatly needed information on the chemical makeup of these samples, thereby clarifying formation mechanisms and helping to determine tholin reactive potential. Moreover, functional group characterization could elucidate key differences in tholins generated under different conditions, perhaps helping to answer the question of which tholin is the most ‘Titan-like’. We aim to tackle this daunting problem one functional group at a time, starting with primary amines.

Amines (R-NH₂) are believed to be present in aerosols on Titan (Mahjoub et al., 2012; Raulin et al., 2012), though they have not yet been unambiguously identified. Ammonia (Cui et al., 2009; Yelle et al., 2010) and methanimine (Vuitton et al., 2006; Yelle et al., 2010) have been positively identified on Titan by the Cassini Ion and Neutral Mass Spectrometer (INMS). In tholins, primary and secondary amine IR absorption signatures have been observed in aerosols generated using inductively coupled cold plasma discharge (Imanaka et al., 2004; Khare et al., 2002; McDonald et al., 1994), capacitively coupled RF cold plasma discharge (Gautier et al., 2012a; Mahjoub et al., 2012; Quirico et al., 2008), and A/C spark discharge (Sarker et al., 2003). Small amines have also been detected using mass spectrometry in capacitively coupled RF cold plasma tholins (Carrasco et al., 2012), A/C spark discharge tholins (Somogyi et al., 2005, 2012), microwave plasma discharge tholins (Fujii and Kareev, 2001; Kareev et al., 2000), and in those generated using EUV/VUV irradiation (Imanaka and Smith, 2010). Solid-state NMR analysis of capacitively coupled RF cold plasma tholins also found evidence of C–N single bonds, most likely due to amines in heterocyclic structures (Derenne et al., 2012), and solution-state NMR analysis of A/C cold plasma discharge tholins identified amino groups as well (He et al., 2012b). However, with these methods it is difficult to measure and quantify amine distributions as a function of chain length. A technique that could add this level of detail to analysis of tholins would provide significant insight into the formation mechanisms of Titan’s aerosols. Such a technique could also provide powerful in situ data if included on the next Titan probe.

Microchip capillary electrophoresis (μ CE) is a liquid-based in situ technique that can be used to separate complex mixtures of both charged and neutral species (Landers, 2008). When cou-

pled to laser-induced fluorescence (LIF), this method is capable of ultrasensitive detection of many classes of organic molecules including amino acids, amines, carboxylic acids, aldehydes, ketones, thiols and PAHs (Mora et al., 2012). We recently reported a protocol to detect primary amines using microchip nonaqueous capillary electrophoresis (μ NACE) in ethanol; the nonaqueous solvent allows solubilization of both short- and long-chain amines, as well as the capability to perform analyses at subzero temperatures (Cable et al., 2013). The technique is based on a highly selective chemical reaction in which a fluorescent dye is covalently bound to a primary amine. We can therefore identify primary amines specifically, and provide quantitative information on these amines down to the sub-parts-per-billion level. We have improved this technique to include detection of ammonia and applied it to the analysis of simulated Titan aerosol (tholin) samples from two different laboratories. We comment on observed correlations between primary amine content and tholin formation conditions, in particular chamber pressure and energy source (UV irradiation, cold plasma discharge and spark discharge).

2. Experimental

2.1. Materials

Methylamine (C1) hydrochloride, ethylamine (C2) hydrochloride, propylamine (C3), amylamine (C5), hexylamine (C6), nonylamine (C9), hexadecylamine (C16) and octadecylamine (C18) were purchased from Sigma-Aldrich; 1-dodecylamine (C12) was purchased from Alfa Aesar. All amines were 97% purity or greater, with the exception of hexadecylamine (90%). Ethyl alcohol (99.5%, ACS reagent, absolute) was purchased from Acros Organics. Ammonium acetate (99.99%), tetrabutylammonium acetate (TBAOAc, 97%), triethylamine (Et₃N, 99.5%) and N,N-diisopropylethylamine (DIEA, 99.5%) were purchased from Sigma-Aldrich. Acetic acid (glacial, 17.4 N, 99.9%), dimethylsulfoxide (DMSO, ACS reagent grade) and N,N-dimethylformamide (DMF, ACS reagent grade) were purchased from Fisher Scientific. Pacific Blue succinimidyl ester (PB) was purchased from Invitrogen (Life Technologies Corp.) and stored at –20 °C as a 20 mM solution in DMF. All reagents were used without further purification. All solutions were filtered prior to use

Download English Version:

<https://daneshyari.com/en/article/6429091>

Download Persian Version:

<https://daneshyari.com/article/6429091>

[Daneshyari.com](https://daneshyari.com)