Available online at www.sciencedirect.com

ScienceDirect

International Journal of Mass Spectrometry 272 (2008) 86–90

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

The ion chemistry of methylenimine and propionitrile and their relevance to Titan

Samuel J. Edwards, Colin G. Freeman, Murray J. McEwan*

Department of Chemistry, University of Canterbury, PB 4800 Christchurch, New Zealand

Received 19 September 2007; received in revised form 21 January 2008; accepted 24 January 2008
Available online 6 February 2008

Abstract

We report here the results of a flowing afterglow-selected ion flow tube laboratory study of the ion–molecule reactions of a series of hydrocarbon ions and simple nitrile ions with methylamine, CH_3NH_2, methylenimine, CH_2NH, and propionitrile, C_2H_5CN at room temperature. When an available exchange proton on the reactant ion was present, collision-rate proton transfer was observed in almost all reactions. The work was motivated by recent observations by the ion neutral mass spectrometer aboard the Cassini space craft as it traversed the upper atmosphere of Titan, Saturn's largest satellite.

Keywords: Methylamine; Methylenimine; Propionitrile; Titan; SIFT

1. Introduction

Ever since the discovery in 1944 of a substantial atmosphere on Titan [1], Saturn's largest satellite, there has been a growing interest in its atmospheric chemistry. This interest has heightened with the arrival of the Cassini space craft at Saturn after undergoing orbital insertion in 2004 [2]. The orbiter has a scheduled tour-of-duty of around 4 years which will take it through the upper atmosphere of Titan around 1200 km above the surface on a number of orbits. During these occasions, measurements have been and will be made of Titan's ionosphere using a suite of instruments on board the orbiter [3] including a mass spectrometer (INMS or ion neutral mass spectrometer) which can examine both neutrals and ions [4].

In parallel with Earth's atmosphere, the major component of Titan's atmosphere is nitrogen [5] although there are few other similarities. The minor atmospheric species in Titan's atmosphere are hydrocarbons (mainly methane but also ethane, acetylene, ethylene and others present at mole fractions of less than 2×10^{-5}) [6]. The ion chemistry of N^+ and $N_2{}^+$ with these species is both complex and interwoven [7]. In an effort to unravel the ion chemistry of Titan, a number of laboratory studies of hydrocarbons in a nitrogen environment have been undertaken [8–15]. These laboratory studies have resulted in a model which can be used to provide a quantitative comparison of the *in situ* observations from the Cassini orbiter. The first results from the Cassini INMS instrument have shown that the current model, although accounting for many ion abundances, cannot explain all of them [16,17]. In order to explain the under-reporting of an ion observed at *m*/*z* 30, Vuitton et al. [17] have proposed that a molecule that is likely to be present on Titan but has not yet been observed is methylenimine, CH_2NH (also known as methanimine or formaldimine). Although not directly measured on Titan, the formation of methylenimine has been proposed as a product of the neutral reaction between N (^{2}D) and CH_4 [18] and it is also produced in the reaction of NH with CH_3 [19]. Methylenimine has been observed in the interstellar medium [20]. Methylenimine is not a particularly stable molecule in the laboratory at room temperature as it undergoes rapid condensation at temperatures above −80 °C [21]. In order to evaluate the role played by methylenimine on Titan it is necessary to examine its ion chemistry. We report here the results of an ion–molecule investigation of a series of ions of relevance to Titan with neutral CH_2NH. In addition, higher densities of propionitrile, C_2H_5CN (also known as ethyl cyanide), were required to account for the abundance of an ion at *m*/*z* 56 in the ion mass spectrum on Titan

---

* Corresponding author. Tel.: +64 3 364 2875; fax: +64 3 364 2110.
E-mail address: murray.mcewan@canterbury.ac.nz (M.J. McEwan).

1387-3806/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2008.01.006

[17]. A number of reactions of neutral propionitrile with ions relevant to Titan's ion chemistry have also been investigated in order to broaden our understanding of the ion chemistry model.

2. Experimental

These experiments were undertaken using the flowing afterglow-selected ion flow tube (FA-SIFT) which has been described previously and a detailed description will not be given here [22]. In brief, mass-selected ions are introduced into the flow tube after generation in the flowing afterglow ion source. The product ions formed in ion–molecule reactions taking place in the flow tube between the mass-selected ion and an added neutral reagent are sampled by the quadrupole mass filter at the downstream end of the flow tube. The rate of reaction is normally found from the semi-logarithmic decay of log(reactant ion density) against neutral reagent flow. A modification to this approach was made for methylenimine as the pure reagent was not available as discussed in the next section.

In the present study, methylenimine was synthesized *in situ* from methylamine by pyrolysis at 1400 °C according to the method of Johnson and Lovas [23]. A quartz pyrolysis tube 150 mm long by 10 mm i.d. was electrically heated to temperatures between 1380 and 1425 °C. A small flow of a dilute (typically 1%) mixture of methylamine in helium, was introduced into the quartz pyrolysis tube via a variable leak valve and the heated tube was positioned within 25 cm of the flow tube in which the ion-neutral chemistry took place. The onset of methylenimine production was apparent from an ion product at *m/z* 30, $CH_2NH_2^+$, arising from the reaction of H_3O^+ and CH_2NH. At temperatures below 1000 °C no methylenimine was observed. It was not possible to monitor the absolute flow of methylenimine directly using this method of preparation as only partial conversion of methylamine into methylenimine occurred with typically ∼15% conversion. Trace amounts of other species, HCN and NH_3, were also generated in the pyrolysis reactor but these did not interfere with the reactions observed. In all the reactions studied the predominant neutral reactant was methylamine, CH_3NH_2. It was therefore necessary to investigate the reactions of each ion with methylamine before interpreting the data with methylenimine as obtained using the methylenimine/methylamine mixture.

It was observed that the production of methylenimine was non-linear with flow through the pyrolysis reactor and this non-linearity prevented the determination of absolute reaction rate coefficients. However, as the reaction rate coefficients for methylamine were directly measured for each reaction, relative rates to those for methylamine were found for methylenimine. The absolute uncertainty for all of the rate coefficients measured in this study is estimated at ±30%. The absolute uncertainty in the product branching ratios is estimated at ±15% for methylamine but is significantly larger for methylenimine at ±50%.

The ions generated in this study were produced from microwave discharge in helium of the following neutral reagents: H_3O^+ from H_2O; O_2^+ from oxygen; $C_2H_5^+$ from methane; $C_3H_3^+$ from allene, $C_3H_5^+$ from ethene; $HCNH^+$ from HCN; CH_3CNH^+ from CH_3CN; $C_2H_3CNH^+$ from C_2H_3CN; HC_3NH^+ from HC_3N; $C_5H_5^+$ and $C_7H_7^+$ from cycloheptatriene and $C_4H_3^+$ from C_4H_2. No attempt was made to determine the nature of the reagent ions produced where the formation of isomers was possible. Previous experience using these methods of ion generation would suggest that a mixture of $C_5H_5^+$ and $C_7H_7^+$ isomers were produced from cycloheptatriene, that linear $C_3H_3^+$ was the principal ion generated from allene and that the lowest energy allyl form of $C_3H_5^+$ was produced from ethane. All of the reagents were obtained from commercial sources and purified by several freeze–pump–thaw cycles. The exceptions were HCN, HC_3N and C_4H_2. HCN was prepared by the action of sulfuric acid on KCN [24]. The preparation of HC_3N required two steps. Methyl propiolate was added to liquid ammonia to obtain propiolamide. Dehydration of this amide by P_2O_5 produced cyanoacetylene [25]. C_4H_2 was generated by the reaction of KOH and 1,4-dichloro-2-butyne at 70 °C [26]. Propionitrile (or ethyl cyanide) was obtained in its pure form (99%) from Aldrich and further purified by freeze–pump–thaw iterations and was introduced into the flow tube as a 1% mixture in helium.

3. Results and discussion

The results of the measurements of the reactant ions with methylamine are summarized in Table 1.

All of the reactant ions with the exception of O_2^+ have a transferable proton. The proton affinity of methylamine at 853 kJ mol^{-1} [32] is larger than most of the neutral species from which the ions are derived (an exception is C_5H_4, 1,3-pentadiyne) and proton transfer (when exothermic) occurs essentially at the collision rate as expected. The two hydrocarbon ions $C_2H_5^+$, $C_3H_5^+$ (PAs of $C_2H_4 = 680.5$ kJ mol^{-1} and allene, $C_3H_4 = 775.3$ kJ mol^{-1}) [32] also exhibited an association channel in competition with proton transfer. The rate coefficients for proton transfer from the ions $C_5H_5^+$ and $C_7H_7^+$ were much less than the collision rate which is indicative of endoergonic proton transfer. The neutral products of these reactions were not measured.

The estimated rate coefficients and product ion distributions for the same ions as in Table 1 are summarized in Table 2 for methylenimine.

The PA of methylenimine at 852.9 kJ mol^{-1} [32] is similar to that of methylamine and this similarity is exemplified in the reaction chemistry. The rate coefficients shown are approximate in that the ratio of methylenimine to methylamine in the pyrolysis reactor was estimated from the reaction of H_3O^+. Once the rate coefficients for the reactions of CH_3NH_2 were known, the relative product amplitudes of each ion with methylamine and methylenimine enabled an estimate of the rate coefficient for methylenimine. Rate coefficients of all of the reactions studied, with the exception of $C_5H_5^+$ and $C_7H_7^+$, were indistinguishable from the calculated collision rate [27] and thus the collision rate estimates have been shown in Table 2. The rate coefficients for the two exceptions were obtained again from the relative rate coefficients of these ions with methylamine. It is worth noting that the two hydrocarbon ions, $C_2H_5^+$ and $C_3H_5^+$ which were observed to exhibit rapid association as well as proton

Table 1
Reactions of named ion with methylamine

Reagent ion	Neutral	Products	Branching ratio	k_o[a]	k_c[a,b]	k_{lit}	$-\Delta H_r$[c]
H_3O^+	CH_3NH_2	$CH_3NH_3^+ + H_2O$		2.1	2.4		199
$C_2H_5^+$	CH_3NH_2	$CH_3NH_3^+ + C_2H_4$	0.80	1.9	2.1	1.8[d]	216
		$CH_3NH_2{\cdot}C_2H_5^+$	0.20				
$C_3H_5^+$	CH_3NH_2	$CH_3NH_3^+ + C_3H_4$	0.40	1.9	1.9		121
		$CH_2NH_2^+ + C_3H_6$	0.25				158
		$CH_3NH_2{\cdot}C_3H_5^+$	0.35				
$HCNH^+$	CH_3NH_2	$CH_3NH_3^+ + HCN$		2.0	2.1	~1.0[e]	178
CH_3CNH^+	CH_3NH_2	$CH_3NH_3^+ + CH_3CN$		1.8	1.9		109
$C_2H_3CNH^+$	CH_3NH_2	$CH_3NH_3^+ + C_2H_3CN$		1.7	1.8		102
HC_3NH^+	CH_3NH_2	$CH_3NH_3^+ + HC_3N$		1.6	1.8		143
O_2^+	CH_3NH_2	$CH_3NH_2^+ + O_2$	0.65	1.9	2.0	1.6[f]	531
		$CH_2NH_2^+ + HO_2$	0.35				388
$C_5H_5^+$	CH_3NH_2	$CH_3NH_3^+ + C_5H_4$	0.80	0.25	1.8		−7
		$CH_2NH_2^+ + C_5H_4 + H_2$	0.10				26
		$CH_3NH_2{\cdot}C_5H_5^+$	0.10				
$C_7H_7^+$	CH_3NH_2	$CH_3NH_3^+ + C_7H_6$	0.90	0.018	1.6		
		$CH_3NH_2{\cdot}C_7H_7^+$	0.10				
$C_4H_3^+$	CH_3NH_2	$CH_3NH_3^+ + C_4H_2$	0.65	2.0	1.8		143
		$CH_2NH_2^+ + C_4H_2 + H_2$	0.25				9
		$CH_3NH_2{\cdot}C_4H_3^+$	0.10				

[a] Observed rate coefficient in units of 10^{-9} cm^3 s^{-1}.
[b] Collision rate coefficient calculated using variational transition state theory in Ref. [27].
[c] Energy in kJ mol^{-1}.
[d] Ref. [28].
[e] Ref. [29].
[f] Refs. [30,31].

transfer with methylamine, also showed the same two product channels with methylenimine. That rapid proton transfer did not occur with $C_5H_5^+$ and $C_7H_7^+$ is an indication that these reactions are endoergic although it should be remembered that in all these studies the neutral fragment from the reaction was not identified.

The relatively large proton affinity of methylenimine resulted in proton transfer dominating the chemistry with simple hydrocarbon ions. A similar situation exists with propionitrile which has a PA of 794.1 kJ mol^{-1} [32]. A summary of the reactions of various ions with propionitrile that were measured in this study are presented in Table 3.

Table 2
Reactions of named ion with methylenimine

Reagent ion	Neutral	Products	Branching ratio	k_o[a]	k_c[a,b]	$-\Delta H_r$[c]
H_3O^+	CH_2NH	$CH_2NH_2^+ + H_2O$	1.0	~3.0	3.0	223
$C_2H_5^+$	CH_2NH	$CH_2NH_2^+ + C_2H_4$	0.95	~2.7	2.7	240
		$CH_2NH{\cdot}C_2H_5^+$	0.05			
$C_3H_5^+$	CH_2NH	$CH_2NH_2^+ + C_3H_4$	0.70	~2.5	2.5	145
		$CH_2NH{\cdot}C_3H_5^+$	0.30			
$HCNH^+$	CH_2NH	$CH_2NH_2^+ + HCN$	1.0	~2.7	2.7	202
CH_3CNH^+	CH_2NH	$CH_2NH_2^+ + CH_3CN$	1.0	~2.5	2.5	133
$C_2H_3CNH^+$	CH_2NH	$CH_2NH_2^+ + C_2H_3CN$	1.0	~2.4	2.4	126
HC_3NH^+	CH_2NH	$CH_2NH_2^+ + HC_3N$	1.0	~2.4	2.4	167
O_2^+	CH_2NH	$CH_2NH^+ + O_2$	1.0	~2.6	2.6	555
$C_5H_5^+$	CH_2NH	$CH_2NH_2^+ + C_5H_4$	1.0	~0.32	2.3	17
$C_7H_7^+$	CH_2NH	$CH_2NH_2^+ + C_7H_6$	1.0	~0.034	2.2	
$C_4H_3^+$	CH_2NH	$CH_2NH_2^+ + C_4H_2$	0.80	~2.4	2.4	167
		$CH_2NH{\cdot}C_4H_3^+$	0.20			

[a] Observed rate coefficient in units of 10^{-9} cm^3 s^{-1}.
[b] Calculated using variational transition state theory in Ref. [27].
[c] Energy in kJ mol^{-1}. Calculated using an enthalpy for $CH_2NH_2^+$ from Ref. [33].

Table 3
Reactions of named ion with propionitrile

Reagent ion	Neutral	Products	Branching ratio	k_{obs}[a]	k_{c}[a,b]	klit[a]	$-\Delta H_{\mathrm{r}}$[c]
N^+	C_2H_5CN	$N_2^+ + C_3H_5$	0.55	4.2	4.50		262
		$C_3H_3^+ + N_2 + H_2$	0.20				748
		$C_2H_4CN^+ + NH$	0.25				630
N_2^+	C_2H_5CN	$C_2H_4CN^+ + N_2 + H$	0.65	3.4	5.80		416
		$CH_3^+ + CH_2CN + N_2$	0.20				216
		$C_2H_2^+ + CH_2NH + N_2$	0.15				92
$HCNH^+$	C_2H_5CN	$C_2H_5CNH^+ + HCN$	1.00	4.2	4.50		88
CH_3CNH^+	C_2H_5CN	$C_2H_5CNH^+ + CH_3CN$	0.95	4.3	3.97		20
		$C_2H_5CN{\cdot}CH_3CNH^+$	0.05				
H_3O^+	C_2H_5CN	$C_2H_5CNH^+ + H_2O$	1.00	4.6	5.20		110
$C_2H_2^+$	C_2H_5CN	$C_3H_5^+ + CH_2CN$	>0.95	4.2	4.60	∼2.2[d]	189
		$C_2H_5CNH^+ + C_2H$	<0.05				39
$C_2H_4^+$	C_2H_5CN	$C_2H_5CNH^+ + C_2H_3$	1.00	4.5	4.50	1.8[d]	77
$C_2H_5^+$	C_2H_5CN	$C_2H_5CNH^+ + C_2H_4$	0.95	4.3	4.45		126
		$C_2H_5CN{\cdot}C_2H_5^+$	0.05				
$C_3H_3^+$	C_2H_5CN	$C_2H_5CN{\cdot}C_3H_3^+$	1.00	∼0.3	4		
$C_3H_4^+$	C_2H_5CN	$C_2H_5CNH^+ + C_3H_3$	0.95	3.9	4.00		120
		$C_2H_5CN{\cdot}C_3H_3^+$	0.05				
$C_3H_5^+$	C_2H_5CN	$C_2H_5CNH^+ + C_3H_4$	0.65	4.1	4.00		59
		$C_2H_5CN{\cdot}C_3H_5^+$	0.35				
$C_4H_2^+$	C_2H_5CN	$C_2H_5CN{\cdot}C_4H_2^+$	1.00	3.6	3.80		

[a] Observed rate coefficient in units of $\times 10^{-9}\ \mathrm{cm^3\ s^{-1}}$.
[b] Calculated using variational transition state theory in Ref. [27].
[c] Energy in $\mathrm{kJ\ mol^{-1}}$.
[d] Ref. [34].

Proton transfer occurred at the collision rate for hydrocarbon ions and protonated HCN and CH_3CN, although some termolecular association channels were also able to compete with proton transfer for CH_3CNH^+, $C_2H_5^+$, $C_3H_4^+$ and $C_3H_5^+$.

4. Conclusions

Measurements made by the INMS instrument on board the Cassini orbiter have detected observable concentrations of species which have been deduced to be methylenimine and propionitrile on the basis that ions containing a single N atom have even masses when protonated, whereas closed-shell hydrocarbons have odd masses when protonated [17,35]. The large PAs of both of these species ensure that most of their reaction chemistry is dominated by proton transfer reactions in the Titan environment. From the variety of hydrocarbon ion reactions with methylenimine examined in this work, it is reasonable to assume a peak at *m*/*z* 30 from $CH_2NH_2^+$ might appear in the ion mass spectrum of the Cassini INMS instrument as suggested by Vuitton et al. [17] A similar situation exists for propionitrile where proton transfer reactions of hydrocarbon ions and smaller nitriles result in an ion at *m*/*z* 56 corresponding to $C_2H_5CNH^+$ as suggested by Vuitton et al. [17]. The association products observed in some reactions in this work, arising from collisional-stabilization competing with proton transfer at flow tube pressures, would not be apparent at the much lower pressures encountered by the Cassini orbiter.

Acknowledgement

SJE thanks the Tertiary Education Commission for the award of a Top-Achiever doctoral scholarship.

References

[1] G.P. Kuiper, Astrophys. J. 100 (1944) 378.

[2] M. Fulchignoni, F. Ferri, F. Angrilli, A.J. Ball, A. Bar-Nun, M.A. Barucci, C. Bettanini, G. Bianchini, W. Borucki, G. Colombatti, M. Coradini, A. Coustenis, S. Debei, P. Falkner, G. Fanti, E. Flamini, V. Gaborit, R. Grard, M. Hamelin, A.M. Harri, B. Hathi, I. Jernej, M.R. Leese, A. Lehto, P.F. Lion Stoppato, J.J. López-Moreno, T. Mäkinen, J.A.M. McDonnell, C.P. McKay, G. Molina-Cuberos, F.M. Neubauer, V. Pirronello, R. Rodrigo, B. Saggin, K. Schwingenschuh, A. Seiff, F. Simões, H. Svedhem, T. Tokano, M.C. Towner, R. Trautner, P. Withers, J.C. Zarnecki, Nature 438 (2005) 785.

[3] L.D. Jaffe, L.M. Herrell, J. Spacecraft Rockets 34 (1997) 509.

[4] J.H. Waite Jr., W.S. Lewis, W.T. Kasprzak, V.G. Anicich, B.P. Block, T.E. Cravens, G.G. Fletcher, W.-H. Ip, J.G. Luhmann, R.L. McNutt, H.B. Niemann, J.K. Parejko, R.L. Thorpe, E.M. Walter, R.V. Yelle, Space Sci. Rev. 114 (2004) 113.

[5] R. Hanel, B. Conrath, F.M. Flasar, V. Kunde, W. Maguire, J. Pearl, J. Pirraglia, R. Samuelson, L. Herath, M. Allison, D. Cruikshank, D. Gautier, P. Gierasch, L. Horn, R. Koppany, C. Ponnamperuma, Science 212 (1981) 192.

[6] A. Coustenis, F. Taylor, Titan: The Earth-like Moon, World Scientific Publishing Co. Pte. Ltd., 1999.

[7] M.J. McEwan, V.G. Anicich, Mass Spec. Rev. 26 (2007) 281.

[8] S. Dheandhanoo, R. Johnsen, M.A. Biondi, Planet. Space Sci. 32 (1984) 1301.

[9] V.G. Anicich, W.T. Huntress Jr., M.J. McEwan, J. Phys. Chem. 90 (1986) 2446.

[10] V.G. Anicich, M.J. McEwan, Planet. Space Sci. 45 (1997) 897.

[11] M.J. McEwan, G.B.I. Scott, V.G. Anicich, Int. J. Mass Spectrom. Ion Process. 172 (1998) 209.

[12] J.L. Fox, R.V. Yelle, Geophys. Res. Lett. 24 (1997) 2179.

[13] V.G. Anicich, P.F. Wilson, M.J. McEwan, J. Am. Soc. Mass Spec. 14 (2003) 900.

[14] V.G. Anicich, P.F. Wilson, M.J. McEwan, J. Am. Soc. Mass Spec. 15 (2003) 1148.

[15] V.G. Anicich, P.F. Wilson, M.J. McEwan, J. Am. Soc. Mass Spec. 17 (2006) 544.

[16] T.E. Cravens, I.P. Robertson, J.H. Waite Jr., R.V. Yelle, W.T. Kasprzak, C.N. Keller, S.A. Ledvina, H.B. Niemann, J.G. Luhmann, R.L. McNutt, W.-H. Ip, V. De La Haye, I. Mueller-Wodarg, J.-E. Wahlund, V.G. Anicich, V. Vuitton, Geophys. Res. Lett. 33 (2006) L07105.

[17] V. Vuitton, R.V. Yelle, V.G. Anicich, Astrophys. J. 647 (2006) L175.

[18] N. Balucani, L. Cartechini, A. Bergeat, P. Casavecchia, G.G. Volpi, Eur. Space Agency Spec. Publ. 496 (2001) 159.

[19] P. Redondo, F. Pauzat, Y. Ellinger, Planet. Space Sci. 54 (2006) 181.

[20] J.E. Dickens, W.M. Irvine, C.H. De Vries, M. Ohishi, Astrophys. J. 479 (1992) 307.

[21] B. Braillon, M.C. Larne, J.M. Denis, Nouveau J. Chim. 6 (1982) 121.

[22] D.B. Milligan, D.A. Fairley, C.G. Freeman, M.J. McEwan, Int. J. Mass Spectrom. 202 (2000) 351.

[23] D.R. Johnson, F.J. Lovas, Chem. Phys. Lett. 15 (1972) 65.

[24] H. Melville, B.G. Gowenlock, Experimental Methods in Gas Reactions, MacMillan, London, 1964.

[25] (a) F.A. Miller, D.H. Mellon, Spectrochim. Acta 23A (1967) 1415;
(b) A.D. Sen, W.T. Huntress, V.G. Anicich, M.J. McEwan, A.B. Denison, J. Chem. Phys. 94 (1991) 5464.

[26] L. Brandsma, Preparative Acetylinic Chemistry, Elsevier Science Publishing BV, New York, 1988.

[27] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.

[28] T. Su, M.T. Bowers, Int. J. Mass Spec. Ion Phys. 12 (1973) 347.

[29] J.A. Herman, K. Herman, T.B. McMahon, J. Am. Soc. Mass Spec. 2 (1990) 220.

[30] D.M. Jackson, N.J. Stibrich, N.G. Adams, L.M. Babcock, Int. J. Mass Spec. 243 (2005) 243.

[31] P. Spanel, D. Smith, Int. J. Mass Spec. 176 (1998) 203.

[32] NIST webbook, webbook.nist.gov/chemistry/.

[33] G. De Oliveira, J.M.L. Martin, I.K.C. Silwal, J.F. Liebman, J. Comput. Chem. 22 (2001) 1297.

[34] J.L. Franklin, Y. Wada, P. Natalis, P.M. Hierl, J. Phys. Chem. 70 (1966) 2353.

[35] V. Vuitton, R.V. Yelle, M.J. McEwan, Icarus 191 (2007) 722.