the relatively crude method of energy scale calibration of the early work. Also, the cross-section is about one order of magnitude lower than the value previously estimated (9.4×10^{-18} versus 2.0×10^{-16} cm^2). Finally, dissociative electron attachment to H_2 (Krishnakumar et al., 2011), CH_3CCH (Janečková et al., 2012), NH_3 (Rawat et al., 2008), HNC (Chourou and Orel, 2009) and C_4N_2 (Graupner et al., 2008) are now included, as some data became available since our previous publication.

The radiative electron attachment rate coefficients are essentially the same as those presented in Table 2 of Vuitton et al. (2009), with the exception of those for H (Stancil and Dalgarno, 1998), C_4H, C_6H (Carelli et al., 2013) and C_5N (Walsh et al., 2009), which have been updated. The changes made for the radiative electron attachment rates are not significant (factor of 2 at most).

Ion-Neutral Reactions. Ion-neutral reactions are presented in Table B.18. Some reaction rates have been updated since Vuitton et al. (2009): Biennier et al. (2014); Martinez et al. (2010), Su & Chesnavich at 150 K (cf. positive ions).

Mackay et al. (1977) measured the rate coefficient for the proton transfer reaction of H^- with C_2H_2 and reported k = $4.4 \pm 1.1 \times 10^{-9}$ cm^3 s^{-1} , a value that we used in Vuitton et al. (2009). Recently, Martinez et al. (2010) obtained k = $3.1 \pm 0.9 \times 10^{-9}$ cm^3 s^{-1} with a similar technique. Although the measurements overlap within combined error bars, the faster rate of Mackay et al. (1977) can be rationalized by the presence of acetone (used to safely store acetylene) as a contaminant in their experiment and we prefer the recent rate of Martinez et al. (2010).

Because HCN is less acidic than HC_3N, we assumed in Vuitton et al. (2009) that the products of the reaction between CN^- and HC_3N are C_3N^- and HCN and that the reaction occurs at every collision. This assumption has since been validated experimentally (Biennier et al., 2014).

We finally include the reaction of C_4H^- and C_6H^- with N atoms, which primarily form CN^- but are rather slow, with rate coefficients close to 10^{-11} cm^3 s^{-1} (Eichelberger et al., 2007).

Negative Ion Loss. Loss mechanisms for negative ions include photodetachment (cf. Table B.12), recombination with positive ions (cf. Table B.17) and associative detachment with neutrals (cf. Table B.19).

For the photodetachment calculations, we adopt a cross-section σ (cm^2) that depends on the photon energy ϵ (eV), according to the empirical formula:

$$\text{for } \epsilon \geq \text{EA}, \ \sigma = \sigma_\infty (1 - EA/\epsilon)^{0.5}, \tag{E24}$$

where σ_∞ denotes the asymptotic cross-section (cm^2) for large photon energies and EA the electron affinity (eV) of the corresponding neutral (Millar et al., 2007). Ion traps have recently been successfully employed to study absolute photodetachement cross-sections for O^- and OH^- (Hlavenka et al., 2009), C_2H^-, C_4H^- and C_6H^- (Best et al., 2011), and CN^- and C_3N^- (Kumar et al., 2013).

For these ions, σ_∞ is derived from fits to the measured cross-sections using Equation (E24) and literature electron affinities. For the other ions for which no experimental data are available, we assume σ_∞ to be equal to 10^{-17} cm^2. The electron affinities and asymptotic cross-section values are given in Table (B.12).

The parameterization of Hickman (1979) for the recombination of negative with positive ions has been revised by Miller et al. (2012), following a new set of measurements. We therefore use the updated expression,

$$k = 2.8 \times 10^{-7} EA^{-0.13} \mu^{-0.5} (T/300)^{-0.9} \ \mathrm{cm^3 s^{-1}}, \tag{E25}$$

where EA is the electron affinity of the corresponding neutral, μ is the reduced mass of the collision partners and T is the temperature of the gas. For the ions of interest here, we obtain rate coefficients varying from 5×10^{-8} to 3×10^{-7} cm^3 s^{-1} at 300 K.

We now consider reaction products and, in the absence of data, we use the general scheme: $A^- + BH^+ \rightarrow A + B + H$. In the case of $HCNH^+$, it is assumed that the product is only HCN (no HNC), the most stable isomer (cf. Table B.20).

We consider associative detachment with H and CH_3 as in Vuitton et al. (2009), and now also include reaction with N atoms that exhibit an abundance similar to CH_3 in the ionosphere. Gerlich et al. (2012) studied the formation of H_2 via associative detachment in H^- + H collisions between 10 and 135 K and reports a rate coefficient of 5.5×10^{-9} cm^3 s^{-1} at 135 K, which we prefer to the room temperature value of Fehsenfeld et al. (1973).

We also update the rate coefficients for CN^-, C_3N^- and C_5N^- with H atoms (Yang et al., 2011; Snow et al., 2009). For CN^-, the reported rate coefficient (6.3×10^{-10} cm^3 s^{-1}) agrees well with the previous results of Fehsenfeld et al. (1973): 8×10^{-10} cm^3 s^{-1} $\pm$ factor of 2. We note that in Vuitton et al. (2009), we reproduced an incorrect value (1.3×10^{-9} cm^3 s^{-1}) cited in Fehsenfeld (1975). For C_3N^- and C_5N^-, the rate coefficient is a factor of $\sim$2 smaller than the assumption (after Petrie and Herbst (1997)) reported in our previous paper.

The reactions with N atoms use the rate coefficients reported in Eichelberger et al. (2007) and Ferguson (1973) for C_2H^- and OH^-, respectively. For the other ions, we assume that the rate coefficient is the same as that for the reaction with H atoms.

Again, we now consider reaction products and, in the absence of data, use the general scheme: $A^- + B \rightarrow AB + e^-$. In the case of C_3H_4, it is assumed that the products are equal amounts of CH_3CCH and CH_2CCH_2 (cf. Table B.14).

2.7.4. ^{15}N Species

In order to take into account ^{15}N bearing species, we start from our ^{14}N chemistry and generate analogous reactions in which ^{14}N is replaced by ^{15}N. Because they do not impact nitrogen chemistry, we do not include reactions of ^{15}N species with oxygen species and negative ions. Reactions in which both reactants contain nitrogen or in which a species contains more than one nitrogen

Table B.12: Mass-to-charge (m/z), electron affinities (EA) and asymptotic cross-sections σ_0 used in the calculation of the photodetachment cross-sections.

Ion species	m/z (u)	EA (eV)	σ_0 (cm^2)	Ref.
H^-	1	0.75	1.0×10^{-17}	[1, 2]
CH_2^-	14	0.65	1.0×10^{-17}	[3, 2]
CH_3^-	15	0.08	1.0×10^{-17}	[4, 2]
C_2H^-	25	3.0	8.8×10^{-18}	[5]
C_4H^-	49	3.6	7.7×10^{-18}	[6, 5]
C_6H^-	73	3.8	4.8×10^{-18}	[6, 5]
CN^-	26	3.9	2.8×10^{-17}	[7, 8]
C_3N^-	50	4.3	5.2×10^{-17}	[9, 8]
C_5N^-	74	4.5	1.0×10^{-17}	[9, 2]
O^-	16	1.5	1.2×10^{-17}	[1, 10]
OH^-	17	1.8	3.3×10^{-17}	[11, 10]

Notes. The asymptotic cross-sections for O^- and OH^- are derived from fits to Eq. (E.15) using the literature electron affinities shown in column 2, and measured cross-sections at 1.87 and 2.33 eV for O^- and 1.87 and 1.96 eV for OH^- (cf. [10]).

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