# Kinetics of suprathermal hydrogen atom reactions with saturated hydrides in planetary and satellite atmospheres

Richard J. Morton, Ralf I. Kaiser*

*Department of Chemistry, University of York, YO10 5DD, UK*

## Abstract

The kinetics of saturated hydrides methane ($CH_4$), silane ($SiH_4$), germane ($GeH_4$), ammonia ($NH_3$), phosphine ($PH_3$), arsane ($AsH_3$), water ($H_2O$), and hydrogen sulfide ($H_2S$) in the low-temperature atmospheres of Jupiter, Saturn, Uranus, Neptune, Pluto, Titan, and Triton reacting with suprathermal hydrogen atoms were investigated computationally to extract suprathermal rate constants $k(E)$ via an inverse Laplace transformation from experimentally available thermal rate constants $k(T)$. Our data reveal that all suprathermal rate constants range up to $10^{-10}$ cm$^3$ s$^{-1}$, whereas the thermal counterparts are as low as $8 \times 10^{-73}$ cm$^3$ s$^{-1}$. These data demonstrate explicitly a significantly enhanced reactivity of photolytically generated suprathermal hydrogen atoms in the low-temperature planetary and satellite atmospheres and suggest that this hitherto unaccounted reaction class should be included by the planetary modeling community into future photochemical networks of atmospheres of outer solar system planets and their moons.
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*Keywords:* Planetary atmospheres; Non-equilibrium chemistry; Cometary chemistry; Hydrogen atoms; Hydrides

## 1. Introduction

Simple saturated hydrides present important chemical constituents in the atmospheres of outer solar system planets, their moons (Yung and DeMore, 1999), and comets (Rodgers and Charnley, 1998). The Voyager missions, star occulations, and terrestrial-based telescopes identified methane ($CH_4$) in the atmospheres of the four giant planets Jupiter (Sada et al., 1998; Maillard et al., 1995; Encrenaz et al., 1995; Strong et al., 1993; Ortiz et al., 1992; Molina and Moreno, 1992; Satoh and Kawabata 1992; Moreno et al., 1991; Molina and Moreno, 1992), Saturn (Ortiz et al., 1993), Uranus (Baines et al., 1995; Smith et al., 1990), and Neptune (Baines et al., 1995; Baines and Hammel, 1994; Romani et al., 1993; Debergh et al., 1990; Romani and Atreya, 1989), as well as Pluto (Stansberry et al., 1996), Titan (Tokano et al., 2001; Kim et al., 2000; Wilson and Atreya, 2000; Lunine et al., 1999; McKay et al., 1997; Samuelson and Mayo, 1997; Samuelson et al., 1997; Ricard et al., 1995; Karkoschka, 1994; Borysow and Tang, 1993; Thompson et al., 1992; Thompson et al., 1991; Karkoschka, 1998), and Triton (Stansberry et al., 1996; Herbert and Sandel, 1991; Strobel et al., 1990) (Table 1). Germane ($GeH_4$), arsane ($AsH_3$), and ammonia ($NH_3$) have also been found on Jupiter (Molina and Moreno, 1992; Nava et al., 1993; de Pater et al., 2001; Fouchet et al., 2000; Edgington et al., 1998, 1999; Folkner et al., 1998; Roos-Serote et al., 1998; Edgington et al, 1998; Lara et al., 1998; Davis et al., 1997; Griffith et al., 1992; Molina and Moreno, 1992; Ferris et al., 1992; Noll and Larson, 1991) and Saturn (Nava et al., 1993; Chen et al., 1991) with upper limits of $NH_3$ derived in Uranus's (Hofstadter and Muhleman, 1989) and Neptune's atmosphere (Yung and DeMore, 1999). Phosphine ($PH_3$) (Edgington et al., 1998; Lara et al., 1998; Davis et al., 1997; Griffith et al., 1992; Borunov et al., 1995; Orton et al., 2000; Weisstein and Serabyn, 1994; Noll and Larson, 1991; Encrenaz et al., 1996) and water ($H_2O$) (Roos-Serote et al., 1998; Bergin et al., 2000; Simon-Miller et al., 2000; Gibbard et al., 1995; Noll et al., 1995; Delgenio and McGrattan, 1990; Dowling and Ingersoll, 1989; Joiner et al., 1992; Degraauw et al., 1997) are present on all of the four giant planets as well. Hydrogen sulfide ($H_2S$) has only been detected on Jupiter (Yung and DeMore, 1999), but upper limits have been derived for Saturn, Uranus (de Pater

* Corresponding author. Present address: Department of Chemistry, University of Hawaii at Manoa, 2545 The Mall, Honolulu, HI 96822, USA.

*E-mail address:* kaiser@gold.chem.hawaii.edu (R.I. Kaiser).

Table 1
Average relative abundances of simple hydrides in the atmospheres of the outer solar system planets and their moons

|  | Jupiter | Saturn | Uranus | Neptune |
|---|---|---|---|---|
| $CH_4$ | $3.0 \times 10^{-3}$ | $4.5 \times 10^{-3}$ | $2.3 \times 10^{-2a}$ | $2.0 \times 10^{-2b}$ |
| $GeH_4$ | $7.0 \times 10^{-10}$ | $4.0 \times 10^{-10}$ | — | — |
| $NH_3$ | $2.6 \times 10^{-3}$ | $2.0 \times 10^{-4}$ | $< 1.0 \times 10^{-7}$ | $< 6.0 \times 10^{-7c}$ |
| $PH_3$ | $7.0 \times 10^{-7}$ | $1.4 \times 10^{-6}$ | $5.0 \times 10^{7}$ | $3.0 \times 10^{-5}$ |
| $AsH_3$ | $2.2 \times 10^{-10}$ | $3.0 \times 10^{-9}$ | — | — |
| $H_2O$ | $3.0 \times 10^{-5d}$ | $2.0 \times 10^{-7e}$ | $1.2 \times 10^{-8f}$ | $3.5 \times 10^{-9g}$ |
| $H_2S$ | $6.1 \times 10^{-6b}$ | $< 2.0 \times 10^{-7}$ | $< 8.0 \times 10^{-7}$ | $< 3.0 \times 10^{-6}$ |

"<" denotes upper limits. $CH_4$ has also been detected on Pluto (0.03), Titan ($1.3 \times 10^{-2}$), and Triton ($1.7 \times 10^{-24}$).

[a] $2.3 \times 10^{-2}$ in the troposphere, $2.0 \times 10^{-5}$ in the stratosphere.

[b] $< 8.6 \times 10^{-7}$ at 3.6 bar, $6.1 \times 10^{-6}$ at 8.7 bar, $6.7 \times 10^{-5}$ at $p > 16$ bar.

[c] At 130 K.

[d] $3.0 \pm 2.0 \times 10^{-5}$ at 6 bar level, $4.0 \pm 1.0 \times 10^{-6}$ at 2–4 bar level.

[e] $2.0 \times 10^{-7}$ $p > 3$ bar in the troposphere.

[f] $5.0–12.0 \times 10^{-9}$ at $p < 0.003$ mbar in the stratosphere.

[g] $1.5–3.5 \times 10^{-9}$ at $p < 0.6$ mbar in the stratosphere.

et al., 1991), and Neptune (de Pater et al., 1991; Deboer and Steffes, 1994). So far, silane ($SiH_4$) has never been discovered in the atmosphere of any solar system planet. Only upper limits of $4 \times 10^{-9}$ have been suggested for the atmosphere of Saturn (Yung and DeMore, 1999).

Although these saturated hydrides are only present in trace amounts, they are important for the chemical evolution of the atmospheres of planets and satellites. For instance, $PH_3$ and related phosphorus-bearing molecules are thought to be responsible for the reddish to brownish color of Jupiter (Griffith et al., 1992; Dowling and Ingersoll, 1989). $CH_4$ is discussed as the key precursor to form the organic haze layers on Titan and Triton. The reactions of hydrogen atoms with saturated hydrides are also of particular importance to the planetary modeling community (Deboer and Steffes, 1994; Samuelson and Mayo, 1997; Ollivier et al., 2000; Orton et al., 2000). The ultimate goal of those investigations is to compute the abundances of molecules in the atmospheres of the planets and their moons and to compare these with actual data derived from infrared, visual, or ultraviolet observations. These models require accurate input data on the reaction products and the rate constants. In general, kinetic models express the temperature-dependent rate constant $k(T)$ as a modified Arrhenius equation (Atkins, 1999):

$$k(T) = AT^{n-1/2}e^{-E_a/RT}, \qquad (1)$$

where $A$ is the pre-exponential factor, $E_a$ the activation energy of the reaction, $R$ the gas constant, $T$ the temperature, where $n$ is a real number. Since the temperatures of the planetary and satellite atmospheres are very low and range between 30 and 165 K (Table 2), rapid chemical reactions should have no or only a small activation energy $E_a$. In particular, the reactions of cyano (CN) and ethynyl ($C_2H$) radicals with unsaturated hydrocarbons were found to be very fast ($k(T) \approx 10^{-10}$ cm$^3$ s$^{-1}$) over a temperature range of 13–293 K (Smith and Rowe, 2000), forming nitriles and complex unsaturated hydrocarbons, respectively, in Titan's

Table 2
The temperatures of the atmospheres of outer solar system planets and their moons

| Planet/Moon | Temperature of the atmosphere (K) |
|---|---|
| Jupiter | 165[a] |
| Saturn | 134[a] |
| Uranus | 76[a] |
| Neptune | 72[a] |
| Pluto | 30−44[b] |
| Titan | 94[a] |
| Triton | 38[c] |

[a] $p = 1$ bar.

[b] $p$ (30 K) = 0.1 μbar; $p$ (44 K) = 500 μbar.

[c] Temperature at the surface, $p$ (38 K) = 17.5 μbar.

atmosphere (Balucani et al., 2000; Kaiser 2002). However, the reactions of hydrogen atoms with simple saturated hydrides of the generic form $MH_n$:

$$MH_n + H \rightarrow MH_{n-1} + H_2 \qquad (2)$$

were postulated to be less important in these low-temperature environments, since they involve significant activation energies (cf. Table 3) (Deboer and Steffes, 1994; Samuelson and Mayo, 1997).

The activation energies cover a range from 5.97 kJ mol$^{-1}$ for $H/AsH_3$ to 85.22 kJ mol$^{-1}$ for the $H/H_2O$ system. Since 11604.5 K is equivalent to 96.5 kJ mol$^{-1}$, the average temperature equivalent of these activation barriers is calculated to lie between 696 and 10,212 K on average. Those figures make it exceptionally clear that thermal reactions of the generic form of Eq. (2) are deemed to be less important in low-temperature planetary and satellite atmospheres. However, these models only consider reactions of thermal hydrogen atoms, but do not account for the reactivity of non-equilibrium (suprathermal) hydrogen atoms with saturated hydrides. Suprathermal species can be generated in

Table 3
Coefficients of the Arrhenius equation (1) of a bimolecular reaction (2) of simple hydrides with atomic hydrogen to form molecular hydrogen (Heyl, 1990; Mallard, 1994)

| Hydride | $A$ (cm³ s⁻¹) | $n$ | $E_a$ (kJ mol⁻¹) | $E_a$ (eV) | $E_a$ (Å)[a] |
|---|---|---|---|---|---|
| $CH_4$ | $1.00 \times 10^{-10}$ | 0.50 | 48.22 | 0.50 | 24,808 |
| $SiH_4$ | $2.30 \times 10^{-11}$ | 0.50 | 11.64 | 0.12 | 102,771 |
| $GeH_4$ | $1.94 \times 10^{-10}$ | 0.50 | 9.40 | 0.10 | 127,329 |
| $NH_3$ | $1.21 \times 10^{-10}$ | 0.50 | 57.50 | 0.60 | 20,804 |
| $PH_3$ | $4.50 \times 10^{-11}$ | 0.50 | 6.14 | 0.06 | 194,703 |
| $AsH_3$ | $2.57 \times 10^{-10}$ | 0.50 | 5.97 | 0.06 | 200,396 |
| $H_2O$ | $1.50 \times 10^{-10}$ | 0.50 | 85.22 | 0.88 | 14,038 |
| $H_2S$ | $1.50 \times 10^{-11}$ | 0.50 | 7.07 | 0.07 | 169,276 |

[a]Wavelength equivalent of activation energy.

Table 4
Solar spectral irradiance at 1 AU (1 astronomical unit (AU) = 1.496 × $10^{11}$ m)

| Wavelength (Å) | Fraction of energy flux | Photon flux (cm⁻² s⁻¹) |
|---|---|---|
| 1200 | $4.4 \times 10^{-6}$ | $2.0 \times 10^{11}$ |
| 2000 | $8.1 \times 10^{-5}$ | $1.1 \times 10^{13}$ |
| 2500 | $1.9 \times 10^{-3}$ | $2.5 \times 10^{14}$ |
| 3000 | $1.2 \times 10^{-2}$ | $2.3 \times 10^{15}$ |
| 3500 | $4.5 \times 10^{-2}$ | $9.1 \times 10^{15}$ |
| 4000 | $8.7 \times 10^{-2}$ | $2.0 \times 10^{16}$ |
| 5000 | $2.3 \times 10^{-1}$ | $6.4 \times 10^{16}$ |
| 8000 | $5.6 \times 10^{-1}$ | $2.2 \times 10^{17}$ |

Table 5
Bond energies of simple hydrides

| Bond | Bond energy (kJ mol⁻¹) | Bond energy (eV) | Bond energy (Å)[a] |
|---|---|---|---|
| H–$CH_3$ | 438.9 | 4.5 | 2725.6 |
| H–$SiH_3$ | 384.1 | 4.0 | 3114.4 |
| H–$GeH_3$ | 349.0 | 3.6 | 3427.7 |
| H–$NH_2$ | 452.7 | 4.7 | 2642.5 |
| H–$PH_2$ | 351.0 | 3.6 | 3408.1 |
| H–$AsH_2$ | 319.2 | 3.3 | 3747.7 |
| H–OH | 498.0 | 5.2 | 2402.1 |
| H–SH | 381.6 | 4.0 | 3134.8 |

[a]Wavelength equivalent of activation energy.

the atmospheres of the outer solar system planets and their moons by, for example, solar photons (Table 4) which can photodissociate hydrides to form atomic hydrogen and the corresponding radical (cf. Eq. (3)):

$$NH_3 \xrightarrow{h\nu} NH_2 + H. \qquad (3)$$

Considering reaction (3) as a typical example and accounting for the bond energy (Table 5) as well as momentum and energy conservation, solar photons of 2000 Å can form hydrogen atoms with a kinetic energy of up to 137 kJ mol⁻¹ (1.42 eV). This kinetic energy of a single hydrogen atom would correspond formally to a temperature

of 16,440 K. Therefore, photolytically generated hydrogen atoms are not in thermal equilibrium with the surrounding low-temperature atmospheres. If the kinetic energy of this suprathermal hydrogen atom is larger than the activation energy of a chemical reaction (2), this energy could be used to overcome this barrier. Therefore we expect that reactions of suprathermal hydrogen atoms are faster than their thermal counterparts. Unfortunately, experimental data on suprathermal rate constants are sparse, but nonetheless crucial to understand the chemical evolution of planetary atmospheres and their moons. This paper employs an inverse Laplace transformation (Arfken, 1985; Heyl and Roessler, 1990) to extract the suprathermal rate constants from experimentally available thermal data (cf. Section 2). The thermal rate constants are compared with their suprathermal counterparts, and the implications to planetary modeling and the evolution of the planetary atmospheres are discussed.

## 2. Methodology

In order to study the reactivity of suprathermal hydrogen atoms, it is essential to calculate the rate constant, $k(E)$, for each reaction at well-defined kinetic energy, $E$, of the suprathermal hydrogen atom. The rate constant $k(T)$ of a bimolecular reaction Eq. (2) at a temperature $T$ is an integral folding the energy-dependent reaction cross section $\sigma(E)$ with the velocity distributions of the reactants. For a reaction between two reactants A and B holding the velocities $|\vec{v_A}|$ and $|\vec{v_B}|$, $k(T)$ is given by (Heyl and Roessler, 1990):

$$k(T) = \int_0^\infty \int_0^\infty f_A(|\vec{v_A}|) \cdot f_B(|\vec{v_B}|) \cdot \sigma(E)|\vec{v_A} - \vec{v_B}| \, \mathrm{d}|\vec{v_A}| \, \mathrm{d}|\vec{v_B}|. \qquad (4)$$

Here, $f_A|\vec{v_A}|$ and $f_B|\vec{v_B}|$ are the velocity distributions of species A and B, respectively, $|\vec{v_A} - \vec{v_B}|$ corresponds to the relative velocity vector $|\vec{v_r}|$. Eq. (4) is versatile and allows us to calculate thermal as well as suprathermal reaction rate

constants. For suprathermal reactions, the energy-dependent cross section $\sigma(E)$ is often unknown. In those cases where neither theoretically calculated nor experimentally determined energy-dependent cross sections are available, a simple procedure can be used to derive $\sigma(E)$. This calculates the energy dependent cross section of suprathermal reactions from experimentally available thermal data. Considering a thermal reaction with a species A, the reactants are in thermal equilibrium and have a Maxwell–Boltzmann velocity distribution $f|\vec{v_A}|$:

$$f(|\vec{v_A}|) = 4\pi \cdot \left(\frac{m_A}{2\pi RT}\right)^{3/2} \cdot |\vec{v_A}|^2 \cdot e^{-m_A|\vec{v_A}|^2/2RT}, \quad (5)$$

where $m_A$ the molar mass of reactant A, $R$ the gas constant, $T$ the temperature, and $|\vec{v_A}|$ the velocity of the reactant A. If the reactants are in thermal equilibrium and can be described as a Maxwell–Boltzmann distribution, $k(T)$ calculates via (4) and (5) to

$$k(T) = (\pi\mu)^{1/2}\left(\frac{2}{RT}\right)^{3/2} \int_0^\infty E\sigma(E)\,e^{-E_o/RT}\,dE. \quad (6)$$

Here, $\mu$ is the reduced mass,

$$\mu = \frac{m_A m_B}{m_A + m_B}, \quad (7)$$

$m_A$ the mass of species A, and $m_B$ the mass of species B. The relative energy $E$ is given by

$$E = \frac{\mu}{2}|\vec{v_A} - \vec{v_B}|^2. \quad (8)$$

Eq. (6) is simply the Laplace transformation of the product $E \times \sigma(E)$ (Arfken, 1985) and can generally only be solved analytically. However, if the energy-dependent cross section $\sigma(E)$ follows Eq. (9), then an explicit solution is possible:

$$\sigma(E) = C\frac{(E - E_o)^n}{E}. \quad (9)$$

Here $E_o$ is the entrance barrier of a reaction, $C$ is a constant, and $n$ is an integer. Plugging Eqs. (8) and (9) into (6) and accounting for the integration limits gives:

$$k(T) = C2^{3/2}(\pi\mu)^{-1/2}(RT)^{n-1/2}\Gamma(n+1)\,e^{-E_o/RT} \quad (10)$$

with the Gamma function $\Gamma(n + 1)$ (Lide, 1999). All non-temperature-dependent pre-exponential factors can be combined into a single constant $A$:

$$A = C2^{3/2}(\pi\mu)^{-1/2}(R)^{n-1/2}\Gamma(n+1). \quad (11)$$

Substituting Eq. (11) into Eq. (10) gives

$$k(T) = AT^{n-1/2}\,e^{-E_o/RT}. \quad (12)$$

This equation relates to the classical Arrhenius relationship and differs only in the temperature-dependent pre-exponential factor, $T^{n-1/2}$, and in the entrance barrier, $E_o$, vs. the activation energy $E_a$. The experimentally available $A$ coefficients (Table 3), can be utilized to calculate the constant $C$.

Due to the uniqueness of the Laplacian formalism we can extract energy dependent cross sections for suprathermal reactants from given thermal reaction rates. Since $n = 1/2$ for all reactions of interest (Table 3) we can correlate the thermal rate constant $k(T)$ data via Eq. (12) with the cross section $\sigma(E)$, Eq. (9), to

$$k(T) = Ae^{-E_o/RT} \quad \Leftrightarrow \quad \sigma(E) = C\frac{(E - E_o)^{1/2}}{E}. \quad (13)$$

It is important to note that the correlation between the rate constant $k(T)$ and the cross section $\sigma(E)$ in Eq. (13) must be modified using the experimental activation energy $E_a$. Classically, the latter is defined as the slope of the logarithmic plot of $k(T)$ vs. $1/T$. Heyl and Roessler (1990) calculated the correlation between the experimentally determined activation energy $E_a$ and the entrance barrier $E_o$ to

$$E_a \approx E_o + \left(n - \frac{1}{2}\right)RT. \quad (14)$$

Since for all of the relevant reactions, $n = 1/2$ (cf. Table 3), the values of $E_o$ and $E_a$ are identical. Now we are able to derive an expression for the suprathermal rate constant $k(E)$. The energy-dependent cross section $\sigma(E)$ relates to $k(E)$ via Eq. (15). This relationship also works because the kinetic energy of a hydride is small in comparison to the kinetic energy of a suprathermal hydrogen atom:

$$k(E) = \sigma(E)|\vec{v_r}| = \sigma(E)\sqrt{\frac{2E}{\mu}}. \quad (15)$$

Plugging Eq. (9) into Eq. (15) gives

$$k(E) = C\frac{(E - E_o)^{1/2}}{E}\sqrt{\frac{2E}{\mu}}$$

$$= \frac{A(\pi\mu)^{1/2}(E - E_o)^{1/2}}{2^{3/2}\Gamma(3/2)E}\sqrt{\frac{2E}{\mu}}. \quad (16)$$

Eq. (16) relates $k(E)$ to $A$ and $E$, allowing both to be calculated using the available thermal data (cf. Table 3).

## 3. Results and discussion

### 3.1. Thermal rate constants

Table 6 compiles the thermal rate constants for the reaction of the saturated hydrides with atomic hydrogen (Table 3) calculated for characteristic temperatures of the atmospheres of outer solar system planets and their moons (Table 2).

As evident the calculated thermal rate constants vary significantly from $3.31 \times 10^{-12}$ to $8.26 \times 10^{-73}$ cm$^3$ s$^{-1}$. These very low rate constants are based on the inherent low-temperatures of the planetary atmospheres and the incapability of the reactants to overcome the activation energy. Since fast reactions are classified by a rate constant of about $10^{-10}$ cm$^3$ s$^{-1}$ (cf. Section 1), the reaction of thermal hydrogen with saturated hydrides are expected to be

Table 6
The rate constants $k(T)$ for various reactions of simple saturated hydrides ($cm^3$ $s^{-1}$)

| Hydride | Jupiter | Saturn | Uranus | Neptune |
|---------|---------|--------|--------|---------|
| $CH_4$ | $5.42 \times 10^{-26}$ | $1.59 \times 10^{-29}$ | $7.19 \times 10^{-44}$ | $5.90 \times 10^{-46}$ |
| $GeH_4$ | $2.06 \times 10^{-13}$ | $4.22 \times 10^{-14}$ | $6.80 \times 10^{-17}$ | $2.70 \times 10^{-17}$ |
| $NH_3$ | $5.59 \times 10^{-26}$ | $1.83 \times 10^{-29}$ | $1.30 \times 10^{-43}$ | $1.17 \times 10^{-45}$ |
| $PH_3$ | $5.11 \times 10^{-13}$ | $1.81 \times 10^{-13}$ | $2.69 \times 10^{-15}$ | $1.46 \times 10^{-15}$ |
| $AsH_3$ | $3.31 \times 10^{-12}$ | $1.21 \times 10^{-12}$ | — | — |
| $H_2O$ | $1.57 \times 10^{-37}$ | $9.03 \times 10^{-44}$ | $4.01 \times 10^{-69}$ | $8.26 \times 10^{-73}$ |
| $H_2S$ | $8.69 \times 10^{-14}$ | $2.60 \times 10^{-14}$ | $2.10 \times 10^{-16}$ | $1.00 \times 10^{-16}$ |

Only $CH_4$ has been detected on Pluto, Titan, and Triton. The rate constants are $5.65 \times 10^{-68}$, $1.60 \times 10^{-37}$, and $3.06 \times 10^{-37}$ $cm^3$ $s^{-1}$, respectively. The temperature for Pluto has been taken as 44 K.

Table 7
Reduced mass and constant $C$ for reactions of atomic hydrogen with various hydrides

| Reaction | Reduced mass, $\mu$ (kg mol$^{-1}$) | Constant, $C$ (kg$^{1/2}$ cm$^3$ mol$^{-1/2}$ s$^{-1}$) |
|----------|-----------|----------|
| $CH_4 + H$ | $9.48 \times 10^{-4}$ | $2.18 \times 10^{-12}$ |
| $SiH_4 + H$ | $9.77 \times 10^{-4}$ | $5.08 \times 10^{-13}$ |
| $GeH_4 + H$ | $9.95 \times 10^{-4}$ | $4.33 \times 10^{-12}$ |
| $NH_3 + H$ | $9.52 \times 10^{-4}$ | $2.64 \times 10^{-12}$ |
| $PH_3 + H$ | $9.79 \times 10^{-4}$ | $9.96 \times 10^{-12}$ |
| $AsH_3 + H$ | $9.95 \times 10^{-4}$ | $5.73 \times 10^{-12}$ |
| $H_2O + H$ | $9.55 \times 10^{-4}$ | $3.28 \times 10^{-12}$ |
| $H_2S + H$ | $9.79 \times 10^{-4}$ | $3.32 \times 10^{-12}$ |

very slow. However, the reactions of $PH_3$ and $AsH_3$ with atomic hydrogen on Jupiter and Saturn have reaction rates of $10^{-12}$–$10^{-13}$ $cm^3$ $s^{-1}$. Therefore these reactions might be relevant even in these low-temperature environments. In the following paragraph, these thermal rate constants will be compared with their suprathermal counterparts to determine the relevance of these reactions in the atmosphere of the outer solar system planets and their moons.

### 3.2. Suprathermal rate constants

The suprathermal rate constants $k(E)$ have been calculated using Eq. (16) using reduced masses and constants $C$ as compiled in Table 7. Table 8 compiles suprathermal rate constants at selected kinetic energies of the hydrogen atoms. These data range from $2 \times 10^{-11}$ to $4 \times 10^{-10}$ $cm^3$ $s^{-1}$. Compared to the thermal rate constants, this is at least two orders of magnitude larger than the maximum thermal rate constants calculated of the H/$AsH_3$ system (Table 6). These data alone imply a significant increase in the reactivity of suprathermal hydrogen atoms compared to thermal ones. Plots of thermal and suprathermal rate constants versus the temperature and kinetic energy of the hydrogen atom, respectively, were also prepared (Figs. 1–8). This gives a quantitative and graphical comparison of how the two rate constants $k(E)$ and $k(T)$ vary with a change in kinetic energy and temperature.

These graphs show common features for all systems investigated. The plots of the suprathermal rate constants $k(E)$ start at a well-defined threshold energy, the entrance barrier $E_o$. Below $E_o$, the rate constant $k(E)$ is zero. As the kinetic energy of the suprathermal H atom rises, the $k(E)$ graphs increase steeply reaching a plateau in the region of 0.5–1.0 eV. The curves of the thermal rate constant $k(T)$ versus the temperature form an elongated s-shaped graph each with two points of inflection; these graphs intersect the $k(E)$ plots before reaching the plateau. For each system, even at very low-temperatures $k(T)$ has a finite value. As the temperature increases, the $k(T)$ versus $T$ graphs also reach plateaus; but the underlying rate constants are always lower than the corresponding suprathermal rate constants $k(E)$.

Table 8
Rate constant $k(E)$ of suprathermal hydrogen atoms with various saturated hydrides at selected collision energies

| Hydride | 0.5 eV | 1.0 eV | 1.5 eV | 2.0 eV |
|---------|--------|--------|--------|--------|
| $CH_4$ | n.r. | $7.08 \times 10^{-11}$ | $8.18 \times 10^{-11}$ | $8.67 \times 10^{-11}$ |
| $SiH_4$ | $2.00 \times 10^{-11}$ | $2.16 \times 10^{-11}$ | $2.20 \times 10^{-11}$ | $2.23 \times 10^{-11}$ |
| $GeH_4$ | $1.74 \times 10^{-10}$ | $1.84 \times 10^{-10}$ | $1.88 \times 10^{-10}$ | $1.89 \times 10^{-10}$ |
| $NH_3$ | n.r. | $7.22 \times 10^{-11}$ | $8.84 \times 10^{-11}$ | $9.55 \times 10^{-11}$ |
| $PH_3$ | $4.22 \times 10^{-10}$ | $4.36 \times 10^{-10}$ | $4.41 \times 10^{-10}$ | $4.43 \times 10^{-10}$ |
| $AsH_3$ | $2.41 \times 10^{-10}$ | $2.49 \times 10^{-10}$ | $2.52 \times 10^{-10}$ | $2.53 \times 10^{-10}$ |
| $H_2O$ | n.r. | $5.20 \times 10^{-11}$ | $9.65 \times 10^{-11}$ | $1.12 \times 10^{-10}$ |
| $H_2S$ | $1.39 \times 10^{-10}$ | $1.45 \times 10^{-10}$ | $1.47 \times 10^{-10}$ | $1.47 \times 10^{-10}$ |

n.r. = no reaction.
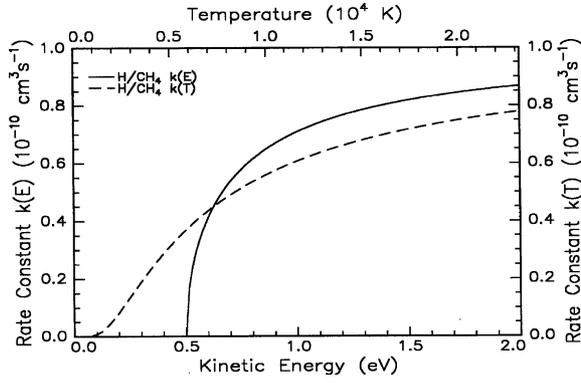
Fig. 1. Energy and temperature dependence of the suprathermal rate constant $k(E)$ and the thermal rate constant $k(T)$ for the H/CH$_4$ system.



Fig. 2. Energy and temperature dependence of the suprathermal rate constant $k(E)$ and the thermal rate constant $k(T)$ for the H/SiH$_4$ system.



Fig. 3. Energy and temperature dependence of the suprathermal rate constant $k(E)$ and the thermal rate constant $k(T)$ for the H/GeH$_4$ system.
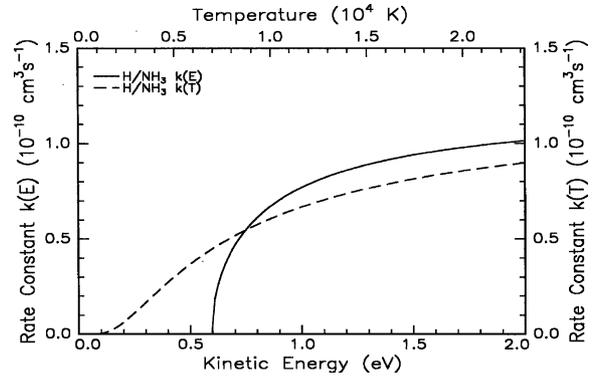


Fig. 4. Energy and temperature dependence of the suprathermal rate constant $k(E)$ and the thermal rate constant $k(T)$ for the H/NH$_3$ system.
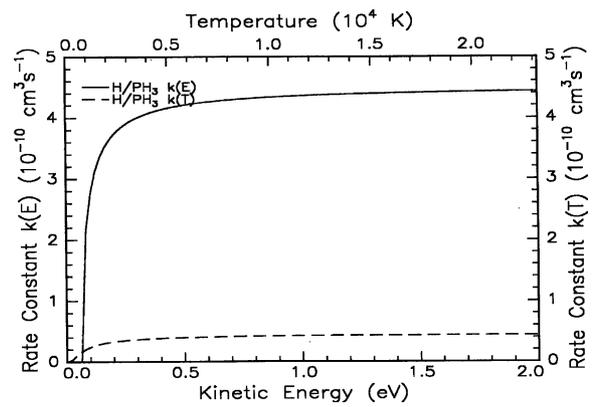


Fig. 5. Energy and temperature dependence of the suprathermal rate constant $k(E)$ and the thermal rate constant $k(T)$ for the H/PH$_3$ system.
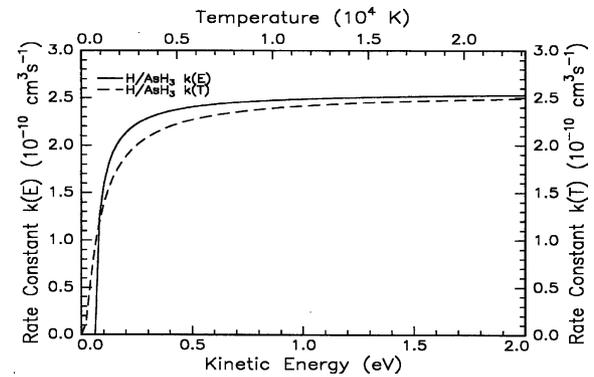


Fig. 6. Energy and temperature dependence of the suprathermal rate constant $k(E)$ and the thermal rate constant $k(T)$ for the H/AsH$_3$ system.

## 4. Conclusions

In this paper, we investigated the kinetics of various saturated hydrides reacting with thermal and suprathermal hydrogen atoms in the low-temperature atmospheres of Jupiter, Saturn, Uranus, Neptune, Pluto, Titan, and Triton. Our data reveal that all suprathermal rate constants are temperature independent and as larger as $10^{-10}$ cm$^3$ s$^{-1}$. Thermal coun-

terparts were found to be—in particular at the prevailing low atmospheric temperatures—as low as $10^{-73}$ cm$^3$ s$^{-1}$. These data alone suggest a significantly enhanced reactivity of suprathermal hydrogen atoms in atmospheres of planets and their satellites. Therefore, future atmospheric models simulating the chemical evolution of outer solar system planets and their moons should include this
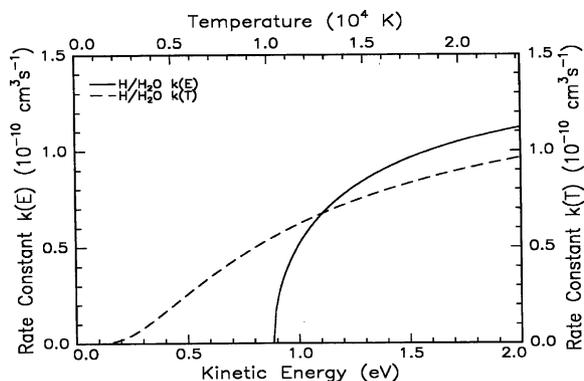
Fig. 7. Energy and temperature dependence of the suprathermal rate constant $k(E)$ and the thermal rate constant $k(T)$ for the $H/H_2O$ system.
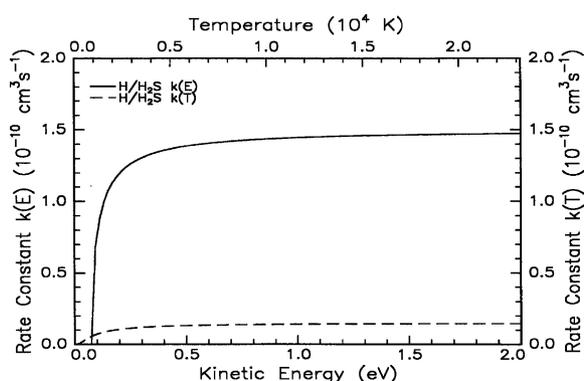


Fig. 8. Energy and temperature dependence of the suprathermal rate constant $k(E)$ and the thermal rate constant $k(T)$ for the $H/H_2S$ system.

reaction class. Since suprathermal hydrogen atoms are strongly expected to be generated via photolyses of saturated hydrides themselves or organic molecules, photochemical models need also wavelength-dependent photodissociation cross section and the translational energy distribution of the suprathermal hydrogen atoms. The actual effect on the planetary chemistry depends also on the branching ratio of reactive collisions versus the gravitational escape of the suprathermal hydrogen atoms. These consideration makes it clear that an inclusion of suprathermal pathways into currently existing models is not trivial—but a challenging task for the future.

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