

EXPERIMENTAL DETERMINATION OF THE RATE CONSTANT FOR THE ASSOCIATIVE DETACHMENT REACTION $\text{H}^- + \text{H} \rightarrow \text{H}_2 + e^-$ AT 300 K

OSCAR MARTINEZ JR.¹, ZHIBO YANG¹, NICHOLAS B. BETTS¹, THEODORE P. SNOW^{2,3}, AND VERONICA M. BIERBAUM^{1,3}

¹ Department of Chemistry and Biochemistry, 215 UCB, University of Colorado, Boulder, CO 80309-0215, USA; Oscar.Martinez@colorado.edu, Zhibo.Yang@colorado.edu, Veronica.Bierbaum@colorado.edu

² Department of Astrophysical and Planetary Sciences, 391 UCB, University of Colorado, Boulder, CO 80309-0391, USA; Theodore.Snow@colorado.edu

³ Center for Astrophysics and Space Astronomy, 389 UCB, University of Colorado, Boulder, CO 80309-0389, USA

Received 2009 August 12; accepted 2009 October 5; published 2009 October 22

ABSTRACT

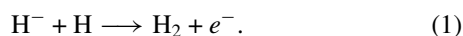
We have determined the rate constant for the associative detachment reaction of hydride ions with hydrogen atoms ($\text{H}^- + \text{H} \rightarrow \text{H}_2 + e^-$) at 300 K to be $2.0 (\pm 0.6) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, where the error bars represent the total absolute error and include 1σ of the measured values; the error analysis is described in the Appendix. Experiments were carried out in a flowing afterglow instrument using the well-characterized reactions of $\text{Cl}^- + \text{H}$ and $\text{OH}^- + \text{H}$ to calibrate the concentration of hydrogen atoms. Our measurement represents a significant improvement over previous determinations and will reduce uncertainties in cosmological models that rely on this reaction rate constant.

Key words: astrochemistry – early universe – molecular processes – methods: laboratory

1. INTRODUCTION

In the early universe, cloud condensation and the formation of protogalaxies and primary stars were contingent on sufficient cooling of primordial gases. Although atomic processes can lower temperatures only to $\sim 10^4$ K, molecules would enable efficient cooling and protogalactic collapse. H_2 is the only molecular species with sufficient concentration to have enabled cooling during this epoch. Processes involved in molecular hydrogen formation and destruction are, therefore, important to models describing the seeding of stars and the forming of protogalaxies. The physics and chemistry in the early universe, as well as the role of molecular hydrogen in structure formation, have been the focus of extensive discussion in the literature (Lepp & Shull 1984; Abel et al. 1997; Galli & Palla 1998; Lepp et al. 2002; Glover & Abel 2008 and references therein).

According to the comprehensive study by Glover et al. (2006) the critical gas-phase reaction in forming H_2 , before dust grains were present to catalyze the process, is the associative detachment reaction of hydride ions, H^- , with hydrogen atoms,



Despite the importance of this reaction, experimental determinations of the rate constant have had large uncertainties. In the earliest measurement, Schmeltekopf et al. (1967) used a newly constructed flowing afterglow instrument in which molecular hydrogen was passed through a microwave discharge, and the resulting hydrogen atom concentration was measured mass-spectrometrically using a chemical titration with nitrogen dioxide. They reported a rate constant value of $1.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, which is reliable to within a factor of 2. Six years later, these researchers (Fehsenfeld et al. 1973) utilized thermal dissociation of H_2 to generate hydrogen atoms, since this method produces fewer excited reactive species; moreover, in contrast to discharge methods, which require an impurity to operate properly, high purity hydrogen was used. Fehsenfeld et al. (1973) used comparison with previously determined, but unspecified, absolute measurements to report a rate constant value of $1.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, again reliable within a factor of 2. In the intervening four decades, this important reaction has not been revisited experimentally. However, Glover et al. (2006) have

shown the dramatic impact of the uncertainty in this rate constant on cosmological models; predictions of the timescale for protogalaxy formation from hot, highly ionized gas within a Hubble time become inconclusive. Thus the propagation of errors in the associative detachment reaction rate constant poses a serious problem to our understanding of the evolution of the early universe.

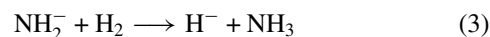
For this reason, we have re-evaluated the rate constant for the $\text{H}^- + \text{H}$ reaction. As described below, we have used thermal dissociation of molecular hydrogen to generate hydrogen atoms, and we have employed exceptionally well-characterized calibration reactions to determine the absolute concentration of hydrogen atoms.

2. EXPERIMENTAL METHODS

A flowing afterglow-selected ion flow tube (FA-SIFT) instrument at the University of Colorado at Boulder was used for these studies. This instrument has been described in detail elsewhere (Van Doren et al. 1987; Bierbaum 2003), and consists of a source flow tube, a mass selection and injection region, a reaction flow tube, and an ion detection system. For these experiments, helium buffer gas (99.99%) is passed through a molecular sieve trap immersed in liquid nitrogen, and admitted to the reaction flow tube at a pressure of ~ 0.4 Torr and a flow rate of $\sim 200 \text{ std cm}^3 \text{ s}^{-1}$. Trace amounts of ammonia gas (NH_3 , Air Products and Chemicals Inc., 99.99%) are added to the upstream region of this reaction flow tube, and H^- ions are formed by electron-impact ionization (70 eV electron energy) via the dissociative attachment process



Amide ions were also formed; therefore, a small flow of molecular hydrogen was added to convert amide ions to hydride ions by the reaction



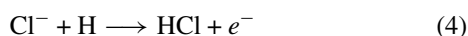
(Otto et al. 2008). The only additional ions in the initial mass spectrum are hydroxide ions, OH^- , formed by trace impurities of oxygen or water vapor; these ions do not complicate the

kinetic analysis for reaction of hydride ions with hydrogen atoms, and in fact, as discussed below, provide an internal calibration of the hydrogen atom concentration.

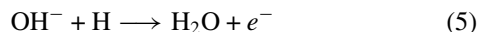
Low ionization emission currents ($\sim 1 \mu\text{A}$) were used to maintain low ion densities; this approach insures that free diffusion conditions prevail throughout the experiment, and that changes in diffusive loss do not occur when negative ions are converted to electrons in the associative detachment process. Sulfur hexafluoride (SF_6) can sometimes be used to scavenge free electrons and prevent changes in diffusive loss at high ion densities; however, this approach is not possible in these experiments, since SF_6 rapidly destroys hydride ions by reactive processes.

We note that attempts to generate H^- ions in the source flow tube, followed by mass selection and injection into the reaction flow tube, were not successful; efficient scattering of hydride ions by helium in the injection process at the Venturi inlet may be the cause of this difficulty. The reactant hydrogen atoms are formed via thermal dissociation. A flow of H_2 gas ($\sim 8 \text{ std cm}^3 \text{ s}^{-1}$, Airgas Inc., 99.999%) is passed through a molecular sieve trap immersed in liquid nitrogen, over a heated tungsten filament (Trainor et al. 1973), and through a second trap and filament assembly. Teflon tubing (0.25 inch ID), used to minimize recombination, then transfers the H atoms from the thermal dissociator into the reaction flow tube; the inlet is positioned 35 cm downstream of the ionizer to allow development of the laminar profile and collisional relaxation of ions, and 70 cm (corresponding to the reaction distance) upstream of the ion sampling orifice to allow adequate reaction time. Dissociation of H_2 is proportional to the voltage applied across the filament (Barckholtz et al. 2001).

The concentration of hydrogen atoms was determined by monitoring the loss of chloride ions or hydroxide ions in the associative detachment reactions with hydrogen atoms. The rate constant for the reaction



has been reported in three studies from the NOAA laboratory in Boulder (Ferguson et al. 1969; Fehsenfeld et al. 1973; Howard et al. 1974), which were in excellent agreement. The third study was exceptionally comprehensive and reported a rate constant of $9.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. These experiments were carried out both in helium and oxygen buffer gases, at pressures between 0.108 and 0.498 Torr, at velocities between 6000 and 8300 cm s^{-1} , and with reaction distances of 40.0 and 81.4 cm. The NOAA laboratory authors used sulfur hexafluoride to scavenge electrons and isothermal calorimetry was used to determine absolute hydrogen atom concentrations that were generated by thermal dissociation. The scatter of nine measurements was about 10% and the total error in the rate constant was reported as $\pm 20\%$. Thus this reaction serves as an excellent calibration for the hydrogen atom concentration. The rate constant for the reaction



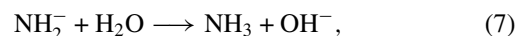
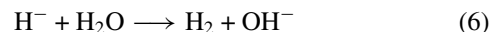
has been reported (Howard et al. 1974) to be $1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ with an accuracy of $\pm 30\%$. Two previous measurements were in good agreement (Ferguson et al. 1969; Fehsenfeld et al. 1973).

For our experiments, chloride ions were made in the source flow tube via electron impact on trace amounts of CCl_4 entrained in helium buffer gas (0.27 Torr); hydroxide ions were generated by adding a mixture of methane (0.04 Torr) and nitrous oxide

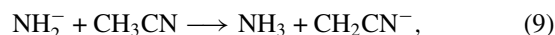
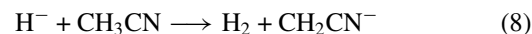
(0.02 Torr) to the buffer gas. The desired ions, either Cl^- or OH^- , were mass selected and injected into the reaction flow tube for reaction with hydrogen atoms. Alternatively as mentioned above, hydroxide ions were present in the reaction flow tube when hydride ions were produced; the loss of H^- and OH^- could be monitored simultaneously upon addition of hydrogen atoms.

3. DISCUSSION

A major challenge in these studies was tuning the detection quadrupole mass filter to transmit extremely low-mass ions; proper tuning of the instrument was achieved with assistance from the staff at Extrel Corporation. A second prerequisite was insuring that the signal intensity near m/z 1 is due to hydride ions, rather than to the "on blast," which is the transmission of all ions when the quadrupole mass filter is set near zero. This issue was explored with ion chemistry. Upon addition of water vapor to the reaction flow tube, the peaks identified as H^- and NH_2^- decreased in intensity due to proton transfer reactions,



while the peak identified as the OH^- product increased in intensity. In contrast, the peak identified as the "on blast" remained relatively constant, since the number density of total ions did not change, although their identities were altered. Similarly, upon addition of acetonitrile (CH_3CN), the peaks identified as H^- and NH_2^- decreased in intensity due to proton transfer,



while the "on blast" remained constant. Thus we are confident that we are generating and detecting hydride ions.

For our study of the reactivity of $\text{H}^- + \text{H}$, 64 measurements were made relative to the reactivity of chloride ions, while 30 measurements were made relative to the reactivity of hydroxide. Hydride ions were generated in the reaction flow tube and their intensity was monitored as the voltage across the tungsten filament in the thermal dissociator, and therefore the hydrogen atom concentration, was increased. Data were recorded for two to ten different voltages. Chloride ions were then formed in the source flow tube and injected into the reaction flow tube, and their intensity was monitored under identical conditions. Since pseudo-first-order conditions exist, the following equations can be written, where k_{Cl^-} is the bimolecular rate constant for $\text{Cl}^- + \text{H}$, k_{H^-} is the bimolecular rate constant for $\text{H}^- + \text{H}$, t represents the reaction time, square brackets indicate concentrations, and the subscript zero indicates initial conditions:

$$\frac{[\text{Cl}^-]}{[\text{Cl}^-]_0} = \exp\{-k_{\text{Cl}^-}[\text{H}]t\} \quad (10)$$

$$\frac{[\text{H}^-]}{[\text{H}^-]_0} = \exp\{-k_{\text{H}^-}[\text{H}]t\}. \quad (11)$$

Our raw data give the value of $[\text{Cl}^-]/[\text{Cl}^-]_0$, and since k_{Cl^-} is known, the value of $[\text{H}]t$ is readily determined. From this value and the experimental ratio $[\text{H}^-]/[\text{H}^-]_0$, the desired rate constant

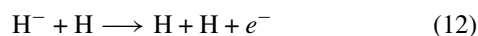
Table 1

Rate Constants for the Reaction of $\text{H}^- + \text{H} \longrightarrow \text{H}_2 + e^-$ ($10^{-9} \text{ cm}^3 \text{ s}^{-1}$)	
Rate Constant	Reference
Experimental values	
2.0 ± 0.6	This work
$1.3 \pm \text{factor of } 2$	Schmeltekopf et al. (1967)
$1.8 \pm \text{factor of } 2$	Fehsenfeld et al. (1973)
Theoretical values	
2.69 (Langevin limit)	Sakimoto (1989)
1.35 (Langevin limit)	Čížek et al. (1998)
1.9	Dalgarno & Browne (1967)
2.0	Browne & Dalgarno (1969)
1.89	Bieniek & Dalgarno (1979)
2.03	Launay et al. (1991)
3.8	Čížek et al. (1998)

for the reaction $\text{H}^- + \text{H}$ is measured. We note that t depends on the pressure and flow of helium, and these values were varied by about 10%; however, $[\text{H}]$ was varied between about 1×10^{10} and $2 \times 10^{11} \text{ cm}^{-3}$, so that the product $[\text{H}]t$ spanned more than an order of magnitude. The average of the 64 measurements of k_{H^-} is $2.11 (\pm 0.32) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ where the error bars represent 1σ of the measurements. No trends of k_{H^-} with experimental parameters were observed. However, reproducibility of results was enhanced by allowing hydrogen atoms to flow for about an hour before accumulating data, and by rapidly interspersing calibration and hydride experiments.

Studies using the reactivity of hydroxide ions as a calibration reaction were carried out in a similar manner; in addition, for some experiments, hydroxide and hydride ions were co-generated and monitored simultaneously as discussed above. The average of the 30 measurements of k_{H^-} is $1.74 (\pm 0.23) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ where the error bars represent 1σ of the measurements. Again, there was no variation with experimental conditions. We report the recommended value of $k_{\text{H}^-} = 2.0 (\pm 0.6) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (the error analysis is outlined in the Appendix). This value is compared to previous experimental determinations in Table 1, as well as to the calculated Langevin collision rate constant determined by the theory of Gioumousis & Stevenson (1958).

The classical Langevin limit calculated here and elsewhere (Sakimoto 1989), $2.69 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, describes the collision rate constant caused by a charge-induced dipole interaction between an ion and a neutral species, which is different from the reaction rate constant. Of the two potential energy surfaces (${}^2\Sigma_u^+$ and ${}^2\Sigma_g^+$) for the reaction $\text{H}^- + \text{H}$, the ${}^2\Sigma_g^+$ potential energy surface, which describes the reaction



has a barrier at low temperatures. Reactions occurring at our experimental temperature do not possess the energy necessary to proceed to the products of reaction (12). This is evident in the extremely small rate constants shown by Dalgarno & Browne (1967) for low temperatures in the range of our experiment. The low-energy thermal collisions at room temperature do not contribute to the reaction due to the repulsive nature of the ${}^2\Sigma_g^+$ potential (Glover et al. 2006), therefore, the reaction rate constant is likely to be no more than half of the Langevin collision rate constant ($1.35 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), which is smaller than our experimental result. However, more sophisticated potential energy functions and different theoretical approaches are needed to properly describe the interaction between hydride

ions and hydrogen atoms during the reaction (Browne & Dalgarno 1969; Bieniek & Dalgarno 1979; Sakimoto 1989; Launay et al. 1991). Dalgarno and coworkers have studied the $\text{H}^- + \text{H}$ associative detachment reaction with a variety of potentials and have found values of the reaction rate constant, $2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Browne & Dalgarno 1969) and $1.89 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Bieniek & Dalgarno 1979), which are very similar to our experimental value at room temperature. Similarly, a study by Launay et al. (1991) gives a value ($2.03 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) consistent with our result at room temperature, as does the radiative dissociation method ($1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) of Dalgarno & Browne (1967). In contrast, Čížek et al. (1998) calculate a reaction rate constant ($3.8 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) at 300 K that exceeds our experimental value by a factor of 2. Several computational studies have addressed the temperature dependence of this reaction (Glover et al. 2006); an accurate temperature variable experimental study would provide a valuable benchmark for theoretical assessments.

4. IMPLICATIONS OF OUR RESULTS

We have measured the rate constant for the associative detachment reaction of $\text{H}^- + \text{H}$ at 300 K as $2.0 (\pm 0.6) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. This measurement represents a refinement of the absolute value, as well as a reduction in the uncertainty compared to previous literature values from a factor of 2 to $\pm 30\%$. The reduced error bar will enable a more accurate modeling and understanding of cooling and protogalaxy formation in the early universe.

Our revised rate constant indicates that H_2 was formed at an earlier epoch than was previously thought. As emphasized by Glover et al. (2006), cooling to collapse a protogalactic halo must occur prior to heating by gravitational disruption due to collision with another protogalactic halo, and must thus occur within a Hubble time. This cooling of the primordial gas clouds prompts collapse and formation of a protogalaxy, and H_2 quadrupole emission is thought to be the dominant cooling mechanism. Therefore, earlier H_2 formation implies earlier star formation and thus earlier heavy element creation in the interiors of massive stars.

We gratefully acknowledge financial support from NASA, the NASA Graduate Student Researchers Program (GSRP), and the National Science Foundation (CHE-0647088). We are grateful to Dr. Daniel Savin for encouraging us to address this important problem. We thank Dr. Carleton J. Howard for his assistance with the hydrogen atoms generation and measurement, and Brian Regel and Kevin Kuchta of Extrel Corporation for their help with our quadrupole mass spectrometer.

APPENDIX

The rate constant values determined from the Cl^- and OH^- calibrations have been weighted and combined according to

$$\bar{k}_{\text{H}^-} = k_{\text{H}^-, \text{Cl}^-} \left(\frac{64}{94} \right) + k_{\text{H}^-, \text{OH}^-} \left(\frac{30}{94} \right), \quad (\text{A1})$$

to give a recommended value of $\bar{k}_{\text{H}^-} = 2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (The symbol $k_{\text{H}^-, \text{Cl}^-}$ represents the rate constant for Equation (1) using Equation (4) as the calibration reaction.). The uncertainties and the number of measurements were weighted according to a

pooled standard deviation:

$$\sigma_{\text{Exp}} = \sqrt{\frac{(64 - 1)\sigma_{\text{H}^+, \text{Cl}^-}^2 + (30 - 1)\sigma_{\text{H}^+, \text{OH}^-}^2}{64 + 30 - 2}}. \quad (\text{A2})$$

Combining the absolute error of the calibration reactions with the reproducibility of our measurements according to

$$\sigma_{\text{Tot}} = \sqrt{\sigma_{\text{Exp}}^2 + \sigma_{\text{Cl}^- \text{-cal}}^2 \left(\frac{64}{94}\right) + \sigma_{\text{OH}^- \text{-cal}}^2 \left(\frac{30}{94}\right)} \quad (\text{A3})$$

gives a total absolute error of $\pm 30\%$.

REFERENCES

- Abel, T., Anninos, P., Zhang, Y., & Norman, M. L. 1997, *New Astron.*, **2**, 181
 Barckholtz, C., Snow, T. P., & Bierbaum, V. M. 2001, *ApJ*, **547**, L171
 Bieniek, R. J., & Dalgarno, A. 1979, *ApJ*, **228**, 635
 Bierbaum, V. M. 2003, in *Encyclopedia of Mass Spectrometry*, ed. P. B. Armentrout (Amsterdam: Elsevier), 98
 Browne, J. C., & Dalgarno, A. 1969, *J. Phys. B: At. Mol. Phys.*, **2**, 885
 Čížek, M., Horáček, J., & Domcke, W. 1998, *J. Phys. B: At. Mol. Opt. Phys.*, **31**, 2571
 Dalgarno, A., & Browne, J. C. 1967, *ApJ*, **149**, 231
 Fehsenfeld, F. C., Howard, C. J., & Ferguson, E. E. 1973, *J. Chem. Phys.*, **58**, 5841
 Ferguson, E. E., Fehsenfeld, F. C., & Schmeltekopf, A. L. 1969, *Adv. At. Mol. Phys.*, **5**, 1
 Galli, D., & Palla, F. 1998, *A&A*, **335**, 403
 Gioumouzis, G., & Stevenson, D. P. 1958, *J. Chem. Phys.*, **29**, 294
 Glover, S. C., Savin, D. W., & Jappsen, A.-K. 2006, *ApJ*, **640**, 553
 Glover, S. C. O., & Abel, T. 2008, *MNRAS*, **388**, 1627
 Howard, C. J., Fehsenfeld, F. C., & McFarland, M. 1974, *J. Chem. Phys.*, **60**, 5086
 Launay, J. M., Le Dourneuf, M., & Zeppen, C. J. 1991, *A&A*, **252**, 842
 Lepp, S., & Shull, J. M. 1984, *ApJ*, **280**, 465
 Lepp, S., Stancil, P. C., & Dalgarno, A. 2002, *J. Phys. B: At. Mol. Opt. Phys.*, **35**, R57
 Otto, R., Mikosch, J., Trippel, S., Weidemüller, M., & Wester, R. 2008, *Phys. Rev. Lett.*, **101**, 063201
 Sakimoto, K. 1989, *Chem. Phys. Lett.*, **164**, 294
 Schmeltekopf, A. L., Fehsenfeld, F. C., & Ferguson, E. E. 1967, *ApJ*, **148**, L155
 Trainor, D. W., Ham, D. O., & Kaufman, F. 1973, *J. Chem. Phys.*, **58**, 4599
 Van Doren, J. M., Barlow, S. E., DePuy, C. H., & Bierbaum, V. M. 1987, *Int. J. Mass Spectrom. Ion Proc.*, **81**, 85