INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 15373–15387

Available online at www.sciencedirect.com

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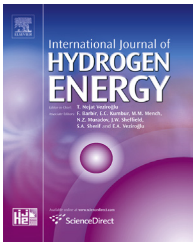
journal homepage: www.elsevier.com/locate/he



Transitioning to a hydrogen economy: Kinetic isotope effects of stratospheric monodeuterated hydrogen accumulation

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ARTICLE INFO

Article history:
Received 27 April 2016
Received in revised form
21 June 2016
Accepted 27 June 2016
Available online 19 July 2016

Keywords:
Hydrogen
Isotope effects
Stratospheric ozone
Computational chemistry

ABSTRACT

This paper investigates for the first time the influence of monodeuterated hydrogen on kinetics of seven stratospheric radical reactions in a consistent, unified manner using the same level of quantum chemistry computational theory. We optimize transition-state structures using MP2 perturbation theory within the finite aug-cc-pVTZ, and show that the evolution to a full-scale hydrogen economy results in the atmospheric accumulation of heavy methane and heavy hydrogen, which can lead to a decrease of polar stratospheric clouds on which ozone is depletion occurs. KIEs imply that increased deuterium in the stratosphere will slow the rate at which HCl reacts with the hydroxyl radical by, approximately, a factor of four. Notwithstanding the improvements of dual-tuning effects of the thermodynamics and kinetics for hydrogen storage materials, these results evidence the need to further investigate, in a systemic rather than piecemeal fashion, the potential impact of anthropogenically released heavy hydrogen on atmospheric radical reactions.

Introduction

Universal consensus has not been achieved regarding the notion that a hydrogen economy or hydrogen itself as a ubiquitous fuel is an efficient and cost-effective means of reducing dependence on fossil fuels. For instance, Shinnar [1] argues that a national distribution system for hydrogen in lieu of the current infrastructure will result in large efficiency losses. Furthermore, some research on the life-cycle efficiency (well-to-wheel) of vehicles using various alternative fuels [2] concludes that vehicles employing hydrogen internal combustion engines from which the hydrogen derives from natural gas have the lowest overall efficiency. The study on well-to-wheel efficiencies also deduces that carbon dioxide emissions would be higher with such vehicles when compared to hybrid gasoline-electric cars. Conceivably, for the transportation sector, the direct use of electricity produced from

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http://dx.doi.org/10.1016/j.ijhydene.2016.06.247

non-carbon sources, namely, hydroelectric and nuclear sources, would be more economical than the production and then subsequent use of hydrogen as a fuel. For cars, arguments can be found supporting the development of electric plug-in hybrids over hydrogen internal combustion engines. However, for larger transportation vehicle mediums such as trucks and planes, battery storage (of energy) may not be feasible. Hydrogen can thus play a potential role if barriers to its storage can be overcome.

The use of hydrogen for commercial consumption necessitates a small volume, efficient delivery storage unit. The unit must resist hydrogen embrittlement. In addition, the hydrogen storage unit and the hydrogen vehicle itself must be of comparable cost and performance to current gasoline and diesel cars and fuel tanks. Thus, the U.S. Department of Energy (DOE) has established a series of targets for hydrogen storage units which, if met, would be analogous to current, conventional fuel tanks. The DOE design targets for 2017 for fuel cell automobile applications include gravimetric and volumetric densities of a hydrogen storage system of 5.5 wt% and 40 kg/m^3, respectively [3]. According to Ross [4], the two most significant targets are the requirement that a charged fuel tank system should contain 6 wt% gravimetric hydrogen density and the requirement that the system should be capable of being recharged at a filling station in less than 5 min. Likewise, the hydrogen should be available for fuel cells at no more than a few atmospheres of pressure without it being necessary to heat the hydrogen store to a temperature of more than 50 °C. Regardless of the storage method, an objective for ensuring conveniently sized containment units is therefore the increase in hydrogen density through volume reduction. The density of hydrogen gas at 298.15 K and 100 kPa is 0.0823 kg/m^3 or 0.0823 g/L [5]. Hence, a decrease in temperature or an increase in pressure is required to decrease molecular hydrogen's occupying volume so as to contain it in a commercially convenient storage unit.

Given that efficient and high density hydrogen storage represents a logjam for hydrogen energy applications, much research has been directed towards the development of new hydrogen storage systems. One development, the hybrid tank system, is a combination of a lightweight high-pressure vessel and a metal hydride, which shows superiority in terms of volumetric and gravimetric hydrogen density over hydrogen storage alloys and compressed hydrogen [6]. AB_2-type Ti-Cr-based alloys are promising candidates, but exhibit relatively high hydrogen desorption pressures and low capacities [7]. Yet, for example, Ti-Cr-Mn-based high-pressure alloys composed of a single C14-type intermetallic (Laves) phase have been prepared for use in a high pressure hybrid MH tank system and their kinetics and cycling stability could meet the required standard for hybrid applications [6]. Thus, the use of metal hydrides offers a possible hydrogen storage system for fuel cell vehicles because high mass densities can be attained with light elements [8]. Various metal hydrides such as LiH, $NaBH_4$, and $LiBH_4$ are used in fuel cells because they can release hydrogen via reactions with water at suitable temperatures. Hydrogen generation via hydrolysis of metal hydrides is found to be a convenient technology for hydrogen production in part because of its safety and its amenability to mild reaction conditions [8–10]. However, some metal hydrides such as $NaBH_4$ exhibit low effective gravimetric capacities for hydrogen storage [11].

In order to overcome low effective gravimetric capacities for hydrogen storage, many researchers in recent years have investigated MgH_2 hydrolysis [11]. Magnesium hydride is a compound with a large hydrogen storage capacity (7.6 wt%) and its storage capacity can increase to 15.2 wt% if MgH_2 hydrolysis uses water produced by a fuel cell [11]. Although such approaches improve the hydrogen yield and the kinetics of hydrogen generation, the lack of control of the rate of hydrogen production can lead to failure in meeting the requirements for commercial application [11]. However, it has been found that the desorption enthalpy change of MgH_2 could be substantially altered by reversibly forming an Mg(In) or Mg(In, Y) solid solution during dehydrogenation. These solid solution systems exhibit slow kinetics [12,13]. Thus, improving its kinetic properties would be significantly beneficial for making use of this thermodynamic tuning effect [14]. Moreover, the high thermodynamic stability of MgH_2 continues to pose a challenge for reducing the hydrogen desorption temperature of Mg-based hydrides. Despite useful efforts, such as alloying and nanostructuring, to tune the thermodynamics of Mg-based alloys, a recent new method by Cao et al. [15] further lowers the stability of MgH_2 by reversibly forming a non-stoichiometric $Mg_{0.95}In_{0.05}$ solid solution.

Light metal hydrides exhibit promising features that make them ideal for hydrogen storage. Yet, challenges remain and in a transition to full hydrogen economy, H_2 leakages into the atmosphere are likely unavoidable. With such promise, supporters of a hydrogen economy predict lower carbon emissions and positive environmental outcomes; however, touting hydrogen as a ‘green’ fuel needs evaluation from many perspectives. If hydrogen, as an energy carrier, will be in wide enough use that it is produced commercially in quantities far greater than it is currently, one will need to consider atmospheric consequences of increased hydrogen accumulation in the stratosphere. If one assumes that in the medium-term, a tethered hydrogen economy is based on the generation of H_2 from fossil-fuels for production strategies for both industrial processes and direct energy services, then leakage and loss rates need to be considered [16]. With hydrogen as a potential future, large-scale energy carrier, unavoidable leaks in the production, storage, delivery and use of H_2, higher atmospheric concentrations of hydrogen could have tropospheric and stratospheric effects. For example, with an excessively high leakage rate, Warwick et al. [17] find that the tropospheric •OH concentration decreases by 10% in a scenario where the hydrogen mixing ratio is increased from 5.5×10^{-1} ppm to 2.3 ppm, which results from a hydrogen energy economy equivalent to today's fossil fuel consumption. In more modest scenarios [17,18], modeling experiments show that increases in anthropogenic hydrogen have small impacts on tropospheric •OH concentrations and that of ozone.

In a full-scale hydrogen economy, the negligible impact of H_2, for example, on tropospheric •OH and ozone from the box models comes from a secondary effect where NO_x emissions are reduced by the replacement of fossil fuels [19]. However, in the transitory phase to full-scale hydrogen economy – a tethered hydrogen economy – hydrogen would be produced