

# Atomic Hydrogen Production from Semi-clathrate Hydrates

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## Supporting Information

**ABSTRACT:** Atomic hydrogen has received recent attention because of its potential role in energy devices, silicon devices, artificial photosynthesis, hydrogen storage, and so forth. Here, we propose a highly efficient route for producing atomic hydrogen using semi-clathrate hydrates. Two major hydrogen radical sources, derived from guest/host materials, are closely examined.

Molecular hydrogen production and storage have been extensively explored over the past three decades.<sup>1</sup> Hydrogen molecules are known to be stable in the confined cages of clathrate hydrates with aid of secondary guests such as tetrahydrofuran (THF) and other cyclic ethers.<sup>2</sup> In contrast, for a single hydrogen atom, few studies have focused on feasible production and storage mechanisms that can operate under mild pressure and temperature conditions.<sup>3</sup> The hydrogen atom, the simplest atom, possesses distinct properties and dynamics due to its quantum mechanical behavior.<sup>4</sup> The application of a clathrate hydrate system for atomic hydrogen recently drew attention because its water framework and various guest molecules have proven to successfully generate and stably imprison atomic hydrogen radicals.<sup>5,6</sup>

The unique geometrical structure and host–guest chemistry of clathrate hydrates may contribute to providing stably encaged sites of reactive radical species. The well-defined hydrogen bond network and host–guest interactions can provide chemically (or physically) stable shelter—even for the smallest radicals. More significantly, we note that the neighboring guest molecules promote the stabilization of atomic hydrogen radicals inside the hydrate structure.<sup>5</sup> In a recent study, we found that classical THF + 17H<sub>2</sub>O + H<sub>2</sub> clathrate hydrate produced atomic hydrogen radicals through the simple  $\gamma$ -ray irradiation of encaged H<sub>2</sub> molecules (*guest-based atomic hydrogen generation*), noting that they were stably captured in small cages.<sup>6</sup> Subsequently, using ionic guest species, Shin et al. also confirmed atomic hydrogen generated from a water framework of  $\gamma$ -irradiated ionic clathrate hydrate (Me<sub>4</sub>NOH + 16H<sub>2</sub>O + N<sub>2</sub>) with the hydrogen radical stabilization effect of N<sub>2</sub> guest molecules in a dodecahedral cage (*host-based atomic hydrogen generation*).<sup>5</sup>

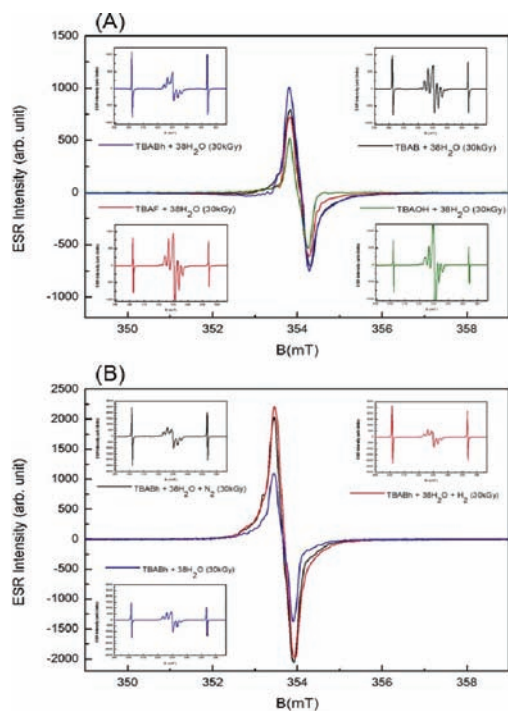
Here, we propose the most effective pathway for producing atomic hydrogen by combining two different hydrogen sources of a host and a guest in a highly complex semi-clathrate hydrate system. For a convincing demonstration of this approach, we choose the tetra-*n*-butylammonium cation (TBA<sup>+</sup>), as this cation forms a semi-clathrate hydrate with various types of anions, such as Br<sup>−</sup>, F<sup>−</sup>, and BH<sub>4</sub><sup>−</sup> when mixed with 38 H<sub>2</sub>O

molecules, as follows: C<sub>16</sub>H<sub>36</sub>N<sup>+</sup>·(Br<sup>−</sup> or F<sup>−</sup> or BH<sub>4</sub><sup>−</sup>)·38H<sub>2</sub>O.<sup>7</sup> In the TBA<sup>+</sup> clathrate hydrate system, anions are strongly incorporated with the host water lattice. In particular, we note that a singly TBA<sup>+</sup> cation occupies four cages.<sup>8</sup> This semi-clathrate hydrate can encage small gaseous molecules that fit into dodecahedral cages.<sup>9</sup>

As the first attempt, we synthesized and  $\gamma$ -ray irradiated the semi-clathrate hydrates of TBAB (Br<sup>−</sup>), TBAF (F<sup>−</sup>), TBAOH (OH<sup>−</sup>), and TBABh (BH<sub>4</sub><sup>−</sup>) with a hydration number of 38. These samples were first tested without non-ionic guest molecules (NIGMs) such as small gaseous molecules. At a dose of 30 kGy of  $\gamma$ -ray irradiation, all four samples produced hydrogen radicals and *n*-Butyl radicals (identified from the peaks shown in Figure S1). All of the samples were weighed before the ESR measurements to estimate the exact amount of their generated radicals. As shown in Figure 1A, the hydrogen radical peak intensity increases in the order of TBAOH, TBAF, and TBAB, reaching its maximum with the TBABh hydrate. For these NIGM-free clathrate hydrates, we simply conjecture that there are two atomic hydrogen radical sources of the ionic guest molecule and host water cage framework. A TBA<sup>+</sup> cation (ionic guest molecule, IGM) is capable of supplying hydrogen radicals inside the cage structure. Furthermore, the water framework of the semi-clathrate hydrate is capable of producing hydrogen radicals. The ability to generate and stabilize hydrogen radicals differs according to the type of anion hosted by the system. The hydroxide ion system cannot hold many hydrogen radicals in the crystal structure. The bromide ion and fluoride ion systems possess similar (slightly higher in the bromide ion system) amounts of hydrogen radicals. The borohydride ion system has the highest maximum hydrogen radical concentration among the four samples. It is interesting to note that the TBABh hydrate system generates the highest concentration of hydrogen radicals. It was assumed that BH<sub>4</sub><sup>−</sup> ions hosted (trapped) in a water framework are partially broken to supply hydrogen radicals. At this stage, to realize a more specific route using the TBA<sup>+</sup> semi-clathrate hydrate, we introduced NIGM (N<sub>2</sub>, H<sub>2</sub>) into the TBABh hydrate and improved hydrogen radical generation greatly compared to the NIGM-free TBABh hydrate (Figure 1B and the full ESR spectrum is shown in Figure S2). It is very interesting to note that the two systems show similar hydrogen radical generation capacities because there is no additional hydrogen radical source in the TBABh + N<sub>2</sub> hydrate. The N<sub>2</sub> molecules in 5<sup>12</sup> cages of TBABh semi-clathrate hydrate act as a hydrogen radical stabilizer for this system as they did in the previously proposed mechanism of extending the lifetime of

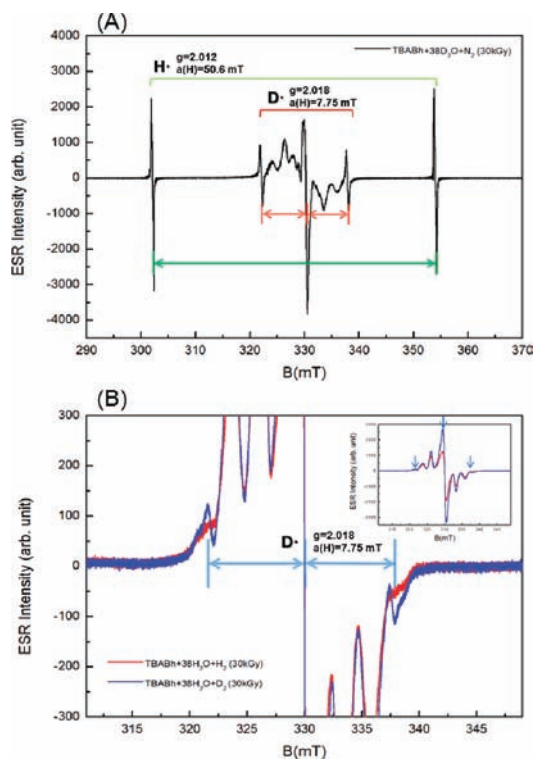
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**Figure 1.** ESR spectrum (hydrogen radical peak region) of (A) the  $\gamma$ -irradiated  $\text{TBA}^+$  hydrate with various anions and (B) the  $\gamma$ -irradiated TBABh hydrate with  $\text{H}_2$ ,  $\text{N}_2$ , and NIGM-free hydrate (insets: full range spectrum).

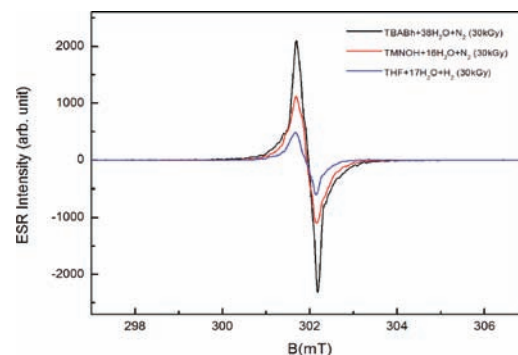
protons from a water framework of ionic clathrate hydrate.<sup>5</sup> We performed additional experiments to determine the true sources of the hydrogen radicals. We prepared a TBABh +  $38\text{D}_2\text{O} + \text{N}_2$  sample and analyzed it using ESR (Figure 2A). We identified from Figure 2A that hydrogen radical peaks ( $g = 2.012$  and  $a(\text{H}) = 50.6$  mT for  $\text{H}^\bullet$ ) come from the splitting of IGM ( $\text{TBA}^+$  ions) in the cage and  $\text{BH}_4^-$  incorporated in the water framework. Moreover, a significant number of deuterium radicals ( $g = 2.018$  and  $a(\text{D}) = 7.75$  mT for  $\text{D}^\bullet$ ) were detected, confirming hydrogen radical generation directly from the water framework. Accordingly, we propose the three different proton sources of the IGM, the water cage framework, and the anion in the clathrate framework. Additionally, we checked the structural stability of the  $\gamma$ -irradiated TBABh +  $\text{N}_2$  hydrate by comparing its X-ray diffraction patterns before and after  $\gamma$ -irradiation (Figure S3). Earlier research revealed that no hydrogen radical peaks were detected in the ESR spectrum of the ionic  $\text{Me}_4\text{NOH}$  clathrate hydrate when  $\text{H}_2$  was enclathrated as NIGM.<sup>5</sup> The  $\text{H}_2$  guest which is known to more charged (i.e., more shielded) than the  $\text{N}_2$  guest in the  $\text{OH}^-$ -incorporated framework strongly inhibits not only electron trapping but also  $\text{H}_2$  splitting.<sup>5</sup> It is, however, surprising to note that, in contrast, the ionic TBABh +  $\text{H}_2$  clathrate hydrate generates a large number of hydrogen radicals. As shown in Figure 2B, the  $\gamma$ -irradiated TBABh +  $\text{D}_2$  sample shows clear D–D cleavage ( $g = 2.019$  and  $a(\text{D}) = 7.78$  mT for  $\text{D}^\bullet$ ). We conclude that hydrogen molecules in dodecahedral cages split to produce additional hydrogen radicals in this system. Thus, four independent contributions for proton sources were confirmed: IGM, water framework, hosted anion, and NIGM. Furthermore, we measured the amount of enclathrated NIGM gas before and after  $\gamma$ -irradiation of the TBABh +  $\text{N}_2$  and TBABh +  $\text{H}_2$  systems through direct release experiments (Table S1). The



**Figure 2.** ESR spectrum (hydrogen radical peak region) of (A) the  $\gamma$ -irradiated  $\text{TBA}^+$  hydrate with various anions and (B) the  $\gamma$ -irradiated TBABh hydrate with  $\text{H}_2$ ,  $\text{N}_2$ , and NIGM-free hydrate (insets: full range spectrum).

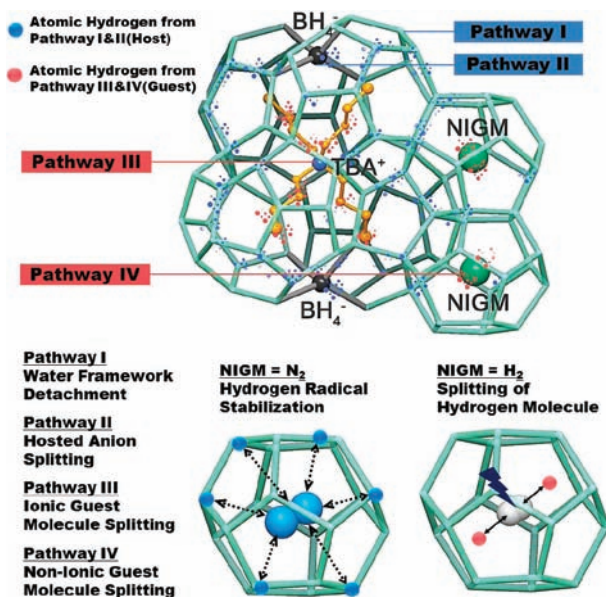
TBABh +  $\text{N}_2$  comprised NIGM gases slightly more compared to TBABh +  $\text{H}_2$ . The amount of enclathrated NIGM molecules affected the overall hydrogen radicals contained in the system. There was no loss of NIGM in both cases during the  $\gamma$ -irradiation process.

Ultimately, the hydrogen radical generation power of the present system (TBABh +  $\text{N}_2$  hydrate) was compared with that of a previous hydrate system in the authors' research: THF +  $\text{H}_2$  hydrate,<sup>6</sup>  $\text{Me}_4\text{NOH} + \text{N}_2$  hydrate.<sup>5</sup> The quantity of hydrogen radicals produced and stabilized in the TBABh +  $\text{N}_2$  hydrate is much greater than that in two earlier systems (Figure 3 and the full ESR spectrum is in Figure S4). Thus, the TBABh +  $\text{N}_2$  hydrate showed the most effective and powerful hydrogen radical generation capacity by combining the pathway of the guest splitting strategy from the THF +  $\text{H}_2$  hydrate and the host detachment strategy from the  $\text{Me}_4\text{NOH} + \text{N}_2$  hydrate.



**Figure 3.** Hydrogen radical generation power of each clathrate hydrate system.

Furthermore,  $\gamma$ -ray irradiation of the TBABh + N<sub>2</sub> or H<sub>2</sub> hydrate led to the discovery of two new pathways: the IGM (TBA<sup>+</sup>) splitting pathway (classified as the guest splitting pathway) and the hosted anion splitting pathway (classified as the host detachment pathway). Accordingly, the TBABh + N<sub>2</sub> or the H<sub>2</sub> hydrate system serves to generate a great number of hydrogen radicals in the clathrate hydrate system. It is worthwhile to note that the formation condition of the TBABh + N<sub>2</sub> system is much milder compared to previous systems (Figure S5). Thus, this semi-clathrate hydrate appears to be most advantageous and promising as a hydrogen radical generator. The atomic hydrogen generation pathways discovered in this study are illustrated in Figure 4. The key findings



**Figure 4.** Visualization of various hydrogen radical generation pathways in the TBABh semi-clathrate hydrate (upper) and two different scenarios depending on NIGM type (down).

from this study are expected to make a meaningful contribution to the understanding of the complex physicochemical characteristics of clathrate hydrates and their applications in hydrogen storage and artificial photosynthesis. It becomes essential to define the possible “sink” pathways (radical decay pathway) of the many hydrogen radicals produced from different pathways in subsequent research. Most of the hydrogen radicals would be annealed back to their initial sources unless special types of external forces (e.g., electrical and physical forces) are exerted in the system. Some hydrogen radicals could migrate through hydrate cages to anneal in different pathways.<sup>4,10</sup> Furthermore, highly reactive hydrogen radical generation in the clathrate hydrate system suggests a preliminary concept for a hydrate-based icy-nanoreactor and a more extensive application of hydrate to energy devices or functional materials. Our next goal is to utilize the massive number of hydrogen radicals generated from semi-clathrate hydrates in the production of methanol and energy gases (CH<sub>4</sub> or H<sub>2</sub>) or in the synthesis of proton-conducting materials through the exertion of various external forces to “active” clathrate hydrates (massive hydrogen radical bearing hydrate). The controlled tuning of sink pathways would enable us to utilize the hydrogen radicals as valuable energy resources.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental methods, full spectrum of the presented ESR data, XRD pattern data, phase equilibrium data, and gas release experiment data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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