Direct observation of atomic hydrogen generated from the water framework of clathrate hydrates†

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We demonstrate that the N_2-induced ionic hydrate system can be a solution to produce the hydrogen radical from water without direct energy sources such as H_2 and CH_4.

The properties and dynamics of single hydrogen atoms are of interest due to their inherent quantum mechanical behavior; thus, their stable observation is a key issue in hydrogen studies. However, they are usually generated and stabilized by high-energy irradiation only at very low temperatures.[1] Remarkably, Yeon et al.[2] demonstrated that icy organic hydrates, which contain small cages that can trap guest molecules, can be used to create and trap hydrogen atomic radicals at much higher temperatures in a previous study. The stable existence of an isolated single hydrogen molecule in water–ice matrices might provide significant advantages in exploring atomic hydrogen as a quantum medium. However, additional in-depth investigations of the production, stabilization, and dynamics of atomic hydrogen in clathrate hydrate have not been done apart from a small number of studies based on theoretical calculations or extremely high pressure condition.[3]

For the generation of hydrogen atomic radicals, the following two approaches can be considered. First, the easiest and most convenient means is to use H_2, CH_4, or other hydrocarbons which have detachable hydrogen atoms by X- or γ-irradiation.[2,4] However, the source cost can be considerable. Second, water, the most abundant substance on earth, might be the most recommendable radical source both economically and environmentally. Thus, a key task here is to find a possible route for radicalizing water molecules. There are two structural types of water molecules in the crystalline solid form: pure ice with an amorphous or a hexagonal structure, and the host water framework of clathrate hydrates. Unfortunately, the pure ice irradiated by a γ-ray source fails to generate hydrogen atomic radicals (Fig. S1, ESI†).[5] The difficulty related to bond breakage and stable radical storage in the pure ice lattice implies that water molecules must be restructured to form host lattices with the aid of what are termed 'guest' molecules, which may greatly affect the host–host and host–guest interactions.

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Accordingly, we attempted to test the 'ice-like' clathrate hydrate materials as hydrogen radical generating sources.

As the first attempt, we chose the ionic clathrate hydrate system, composed of tetramethylammonium cations (Me_4N^+), OH^- incorporated host, and non-ionic guest molecules (NIGM), in order to produce the hydrogen radical from host water. In a previous study,[6] we demonstrated the charge transfer phenomenon from a charged host to the non-ionic guest in the Me_4NOH + NIGM hydrate system. Unusual host–guest interaction in this ionic system can lead to the radicalization of the host water framework. We initially prepared three Me_4NOH hydrate samples of N_2, H_2, and O_2, respectively. Including NIGM is known to transform the Me_4NOH hydrate system into cubic $Fd3m$, which is known as structure-II (sII) through its occupation of the newly created cages with a hydration number of sixteen.[6] High-resolution X-ray powder diffraction (HRPD) patterns verified that prepared samples have the cubic $Fd3m$ lattice, as expected (Fig. S2, ESI†).

In earlier studies, Bednarek et al.[7] detected $CH_3^•$ and $-NCH_2^•$ radicals generated from the X-irradiation of Me_4NOH pentahydrate and observed that the trapped electrons evolve blue coloration. Here, we also checked the ESR spectrum of the γ-irradiated Me_4NOH decahydrate, i.e. NIGM-free hydrate, and obtained a splitting pattern with quite a small atomic hydrogen signal (Fig. S3a, ESI†). Peak broadening of the centered peaks in this ESR spectrum and the blue coloration of the sample (Fig. 1a) confirm that, regardless of the water framework structure, electrons ejected from γ-irradiated H_2O are readily trapped in the host cages comprising Me_4N^+ due to its positive charge.[7] In contrast, the hydroxyl radicals and electrons which fail to be entrapped stably are consumed to react with Me_4N^+ in the cage and eventually, $-NCH_2^•$ and $CH_3^•$ are produced (identified from centered peaks of Fig. S3a (ESI†), $g = 2.0017$ and $a_c(H) = 2.35$ mT for $CH_3^•$; $g = 2.0015$ and $a_α(H) = 2.43$ mT for $-NCH_2^•$). Some of these electrons are considered to form
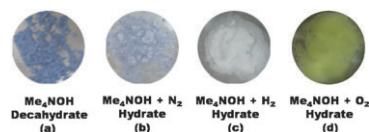

Fig. 1 Color change of γ-irradiated samples. Blue coloration is caused by trapped electrons in the cage including Me_4N^+ and yellow coloration is caused by generation of O_2^-. The molecular electron affinities of NIGMs (58 kcal mol⁻¹, 44 kcal mol⁻¹, and 1 kcal mol⁻¹ for N_2, H_2, and O_2, respectively) affect the interaction between charged host and NIGM.

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hydrogen radicals through reactions with H^+, but the detected signal intensity is quite small.

At this stage, we can simply note that the inclusion of NIGM seems not to seriously affect the radiolysis mechanism of Me_4NOH hydrates, if the charge transfer between the charged host and the NIGM is ignored.[6] Although the inclusion of the NIGM is accompanied with the structural transformation, the $5^{12}6^4$ cage which entraps Me_4N^+ in the newly formed host framework is larger than the $4^6 6^8$ cage which has only one type of vacant site in the β-form of Me_4NOH pentahydrate.[8,9] Such a large cage is sufficient to comprise both electron and cation together. We might here simply conjecture that the H_2 guest separated from Me_4N^+ by the water cage may be split in its independent 5^{12} cage, as the molecular hydrogen in the THF + H_2 hydrate was split into two hydrogen atoms in an aforementioned report.[2]

Next, we examined the radical formation of the Me_4NOH + N_2 hydrate. A large doublet signal representing a hydrogen atomic radical appeared in its ESR spectrum (Fig. S3b, ESI†). This is a surprising result because the N_2 guest itself cannot be a source of the generation of hydrogen atomic radicals. We note here again that the irradiation of hexagonal pure ice only produces hydroxyl radicals, whereas hydrogen atomic radicals are not observed (Fig. S1, ESI†). These experimental findings strongly suggest an uncommon type of interaction between the charged host, water and encaged guest, N_2. In addition, another peculiar phenomenon can be observed, as shown in Fig. S3c (ESI†). Unlike the N_2 molecule, one H_2 molecule can be split into two hydrogen atomic radicals due to γ-irradiation. The findings of a previous study of the γ-irradiated THF + H_2 hydrate[2] supports this expectation. Surprisingly, the present study failed to detect any trace of hydrogen atomic radicals in the ESR spectrum of the Me_4NOH + H_2 hydrate. Regarding the centered peaks indicating $-NCH_2^•$ and $CH_3^•$, the peak broadening induced by the trapped electrons was weakened for the N_2 guest (Fig. S3b, ESI†, $g = 2.0017$ and $a_c(H) = 2.33$ mT for $CH_3^•$; $g = 2.0015$ and $a_\alpha(H) = 2.36$ mT for $-NCH_2^•$), while this peak broadening was not observed for the H_2 guest (Fig. S3c, ESI† $g = 2.0017$ and $a_c(H) = 2.31$ mT for $CH_3^•$; $g = 2.0016$, $a_\alpha(H) = 2.35$ mT, and $a_{remote}(H) = 0.42$ mT for $-NCH_2^•$). Correspondingly, the N_2 sample became lighter blue and H_2 sample was not colored by γ-irradiation (Fig. 1b and c). The Me_4NOH + O_2 hydrate was also tested, but only super-oxide ions with quite a small hydrogen radical doublet were detected, and these did not show any $CH_3^•$ or $-NCH_2^•$ signals (Fig. S3d, ESI†, $g_{xx} = 1.9807$, $g_{yy} = 2.0055$ for O_2^-).[10] These ESR results reflect that the molecular details of NIGMs significantly influence the radiolysis mechanism of Me_4NOH hydrates.

Here, we focus on the interaction between the ionic host and NIGM. In the previous study,[6] charge transfer from the charged host to the NIGM in the Me_4NOH hydrate system was observed. The host electron inclining toward the NIGM might prevent it from being pulled toward Me_4N^+. The degree of charge transfer is considered to depend largely on the unique properties of NIGM, such as the molecular electron affinity. The molecular electron affinities of different NIGMs were computed to be 58 kcal mol^{-1}, 44 kcal mol^{-1}, and 1 kcal mol^{-1} for N_2, H_2, and O_2, respectively. Accordingly, the H_2 guest which is more charged (i.e., more shielded) than the N_2 guest in the OH^-

incorporated framework strongly inhibits not only the electron trapping but also H_2 splitting, while the O_2 guest, expected to be much more charged in the same ionic system due to its electron affinity and reactive nature, prevents the formation of $-NCH_2^•$ and $CH_3^•$ and traps an electron in the $5^{12}6^4$ cage by drawing the host electron into O_2 itself (Fig. S3d, ESI†).[10]

However, why the large amount of hydrogen atomic radicals is generated particularly in the γ-irradiated Me_4NOH + N_2 hydrate remains unexplained. At this point, the urgent task is to determine the actual source of the hydrogen radical, whether they come from the host water or Me_4N^+. Thus, we checked the ESR spectrum again, using deuterium oxide (D_2O) instead of water. The ESR spectra of irradiated $(CH_3)_4NOD$–N_2–D_2O show both a doublet from hydrogen and a triplet from deuterium radicals (Fig. S4a, ESI†). The appearance of a complex peak in the center of the spectrum represents partially deuterated methyl or methylene radicals. The deuterium is known to have a somewhat different coupling constant and nuclear spin number from hydrogen. Thus, we can conclude that the deuterium/hydrogen radicals generated in the N_2-induced clathrate hydrate come from the host water and are in an equilibrium state of proton exchange with $-NCH_2^•$ and $CH_3^•$ in the $5^{12}6^4$ cages. Additionally, the ESR spectrum of the γ-irradiated Me_4NOH + H_2 hydrate was reinvestigated in order to confirm the possibility that hydrogen radicals formed by H_2 splitting are eliminated through reactions with other components, such as hydroxyl radicals, to form water, or with Me_4N^+ to form $-NCH_2^•$ and H_2 again. In this case, deuterium gas (D_2) was used instead of H_2 gas. The ESR spectrum of this γ-irradiated $(CH_3)_4NOH$–D_2–H_2O system is represented in Fig. S4b (ESI†). There is no difference between this spectrum and that of Fig. S3c (ESI†), implying no H–D exchange between $-NCH_2^•$ or $CH_3^•$ in the $5^{12}6^4$ cage and D_2 in the 5^{12} cage. Therefore, the hydrogen molecule encaged in this charged host cannot detach hydrogen atoms from the host water, nor can it be split by γ-irradiation.[11]

In order to understand the impressive hydrogen radical generation when NIGM = N_2, we calculated the proton affinities of N_2, H_2, and O_2. As the experimental temperature was low (77 K) and the NIGM molecules are trapped within the hydrate cages, we expect that the entropic contribution is minimal. We therefore calculated the proton affinities of NIGMs at 0 K. Apparently, the proton affinity of N_2 (-123 kcal mol^{-1}) is much larger than that of H_2 (-106 kcal mol^{-1}) or O_2 (-99 kcal mol^{-1}), and a high relative proton affinity of N_2 can be explained in terms of the favorable electrostatic interaction between the lone pair electrons of N_2 and the proton.[12] Based on these thermochemical data, we propose the following mechanism on the hydrogen radical generation from water molecules of the host cage (Fig. 2). As described above and in the literature,[7] the radiolysis is initiated by the ionization of water molecules into protons, electrons, and hydroxyl radicals, i.e., $H_2O \rightarrow e^- + H^+ + {}^•OH$.

Immediately after this initial ionization, the protons can be stabilized by neighboring water molecules within the cage through a well-defined hydrogen bond network, but most of the time, protons will recombine with electrons and OH radicals to regenerate water molecules. This possibility explains why most of the hydrogen radicals of the γ-irradiated
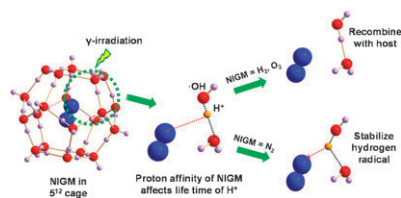
Fig. 2 Stabilization of hydrogen radicals by the catalytic N_2 guest. Proton affinity of N_2 (-123 kcal mol^{-1}) is superior to that of H_2 (-106 kcal mol^{-1}) or O_2 (-99 kcal mol^{-1}).

THF + H_2 hydrate in a previous study[2] did not originate from the host water molecules but came from the guest molecules. When N_2 guest molecules with a high proton affinity are present, however, the initial protons can be further stabilized by these guest molecules that are located remotely from the hydrogen bond network of the host, preventing the recombination of protons into water. The net result is then the extended lifetime of protons that can combine with electrons to yield hydrogen radicals. In other words, since N_2 molecules act as a catalyst for this reaction and there are plenty of proton sources (*i.e.*, water molecules in the cage) and trapped electrons, the Me$_4$NOH hydrate with N_2 can generate the large amount of hydrogen radicals. In addition, our proposed mechanism of the extended lifetime of protons due to N_2 accounts for the experimental observation of the significant H–D exchange data (Fig. S4a, ESI†).

To confirm the N_2 effect of γ-irradiation of the icy framework, we also check the THF + NIGM hydrates as well as simple N_2 and O_2 hydrates having the same crystalline structure of cubic $Fd3m$.[9] All of the samples shown in Fig. 3 were weighed before ESR measurements to estimate and compare their hydrogen radical production ability against each other. As shown in Fig. 3b, the produced hydrogen radical concentration of the THF + N_2 hydrate is much higher than that of pure THF or THF + O_2 hydrates, though it is lower than the THF + H_2 hydrate. Considering that the hydrogen radical in the THF + H_2 hydrate dominantly comes from H_2 itself, this is clear evidence that the N_2 guest can detach the hydrogen atom from the water framework. Additionally, the simple N_2 hydrate also showed this ability of hydrogen atom detachment from the host water, whereas hexagonal ice without any guest molecules and the simple O_2
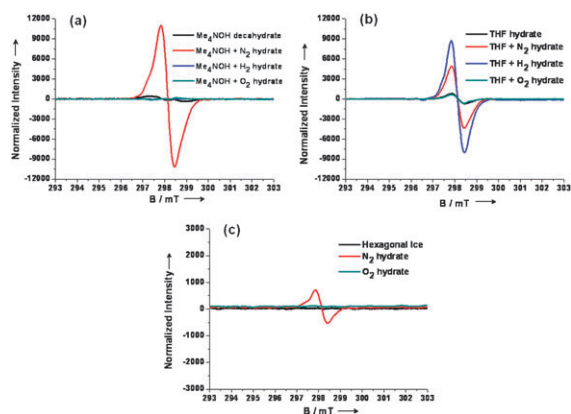
hydrate could not produce hydrogen radicals (Fig. 3c). However, the radical concentration of the simple N_2 hydrate is much lower compared to those of Me$_4$NOH + N_2 and THF + N_2 hydrates. This implies that the existence of a large guest molecule in the $5^{12}6^4$ cage, which is proton-exchangeable with the hydrogen radicals coming from H_2O, is also one of the important factors in the production of hydrogen radicals. With the largest signal of the Me$_4$NOH + N_2 hydrate represented in Fig. 3a, three points, *i.e.*, hydrogen atom detachment by the N_2 guest, stabilization by the proton exchanging equilibrium with a large guest, and the enhancement by the OH$^-$-incorporated ionic host framework, might be essential to produce hydrogen radicals from an icy framework. Accordingly, we can conclude that the N_2-induced ionic hydrate system can be a solution to produce the hydrogen radical without direct energy sources such as H_2 and CH$_4$. The present findings are expected to provide significant contributions to a greater understanding of the complex physicochemical characteristics of clathrate hydrates, although they are preliminary. Hence, additional extensive research including the stability of defects in the hydrate lattice[13] is necessary to synthesize and fabricate the ice-based functional materials and energy devices.

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Fig. 3 Hydrogen radical peaks of γ-irradiated hydrates with normalized intensities by sample weights in ESR spectra.